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Carbon Positions in Uranium Carbides*

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The carbon atom positions in uranium carbides have been determined from neutron diffraction data. UC is face-centered cubic with sodium chloride structure. U_2C_3 is body-centered cubic with space group $I\bar{4}3d$, and carbon atoms have one parameter of 0·295 with carbon–carbon bond distance of 1·295 Å. UC_2 is tetragonal with space group $I4/mmm$, and the carbon atoms have z parameter of 0·388 with carbon–carbon bond distance of 1·34 Å. The metal–carbon bonding is discussed.

Introduction

The structures of uranium carbides, UC, U_2C_3, and UC_2, have been reported (Rundle *et al.*, 1948; Mallett *et al.*, 1951; Litz *et al.*, 1948) from X-ray diffraction data. However, only the uranium atom positions could be determined unequivocally because of the small X-ray scattering power of carbon as compared to uranium. The carbon positions in these carbides have been determined now from neutron diffraction data.

Experimental

The carbides of nominal composition were made by arc melting under helium. The uranium sesquicarbide ingot was heat treated at 1700 °C. for 4 hours to form the U_2C_3 phase. All the carbides were crushed to minus 200 mesh. Table 1 gives the chemical compositions and unit-cell constants determined from X-ray diffraction powder data. The U_2C_3 material contained a minor amount of UC_2 phase and the UC_2 material had a trace of UC.

Table 1. *Compositions and unit-cell constants of* UC, U_2C_3, *and* UC_2 *preparations*

	Analysis *w/o*			
Material	U	C	N	Cell constants (Å)
UC	95·3	4·64	0·04	$a_0 = 4{\cdot}9598 \pm 0{\cdot}0003$
U_2C_3	92·5	7·51	0·008	$a_0 = 8{\cdot}0885 \pm 0{\cdot}0005$
UC_2	91·4	8·39	0·04	$a_0 = 3{\cdot}509 \pm 0{\cdot}003$
				$c_0 = 5{\cdot}980 \pm 0{\cdot}005$

The neutron diffraction data were obtained at the Battelle Research Reactor with neutrons monochromated by a lead crystal to 1·100±0·005 Å. The incident beam was monitored and the diffracted intensity was recorded for preset monitor count at step increments of 0·25° 2θ. The probable counting error was about 2% for diffraction peaks and 3·5% for background. The samples were contained in 0·430 in. diameter aluminum tubes with 0·007 in. wall. The sample height was about 3 in. for a neutron beam of 1 in. height. The spectrometer had a resolution of 1·8° 2θ half breadth, with these samples and with the spectrometer geometry employed. The diffraction data were obtained out to 90° 2θ.

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The integrated intensities were determined after correction for the background from empty sample tubes. The intensities were calibrated by comparison with nickel powder. Values of $|F|^2$ or $\Sigma j|F|^2$ for unresolved reflections were obtained using the normal equation for intensity. Absorption corrections, A_{hkl}, were made from a knowledge of the specimen density, its radius, and the neutron mass absorption coefficient. The temperature factor $\exp[-2B(\sin^2\theta/\lambda^2)]$ was determined for UC from the slope of a plot of $|F|_o^2$ versus $\sin^2\theta/\lambda^2$. The mean temperature factor of UC was used in the calculations of U_2C_3 and UC_2.

Results

UC

Uranium monocarbide, UC, is face-centered cubic with the sodium chloride structure. The observed structure factors agree with the calculated values to 1·5% for reflections from (111) to (440), for scattering factors of $0{\cdot}85\times10^{-12}$ cm. for uranium and $0{\cdot}66\times10^{-12}$ cm. for carbon. The temperature factor B ranged from 0·07 Å^2, for (h00) reflections, to 0·30 Å^2, for (hh0), with a mean value of 0·19 Å^2. The corresponding root mean square atom displacements were 0·03 Å for 100 directions, 0·06 Å for 110 directions and 0·05 Å for mean displacement. Table 4 gives the interatomic distances.

U_2C_3

Uranium sesquicarbide, U_2C_3, had been reported to be body-centered cubic with space group $I\bar{4}3d$ (Mallett *et al.*, 1951). This structure is isomorphous with Pu_2C_3 (Zachariasen, 1952). Both reports agree on positions of the metal atom in 16-fold positions with $x = 0{\cdot}050\pm0{\cdot}003$. In both previous studies by X-ray diffraction, the carbon atom positions were not determined. Zachariasen (1952) proposed that the carbon atoms were in the 24-fold positions, $x, 0, \frac{1}{4}$, with a parameter of 0·28 and a carbon–carbon distance of 1·54 Å.

The neutron intensity data for the U_2C_3 preparation had to be corrected for minor contributions of the UC_2 phase. Because several reflections were incompletely resolved, it was necessary to use neutron intensity data to compare with calculated values of $j|F|^2$. Such calculations were made for parameter variations from 0·270 to 0·300. The minimum R factor

$$\frac{\Sigma[j|F|_o^2 - j|F|_c^2]}{\Sigma j|F|_o^2}$$

was 0·20 for a parameter of $0{\cdot}295\pm0{\cdot}0025$. For parameter value 0·30 the carbon atoms would be closer than the triple-bond distance. Table 2 compares the observed $j|F|^2$ values and those calculated for the parameter 0·295. The possibility of variation in the uranium atom parameter was checked and the R factor increased to 0·25 for ±0·003 variation. Table 4 lists interatomic distances.

Table 2. *Neutron diffraction data for* U_2C_3

d (Å)	hkl	$j\|F\|_o^2$	$j\|F\|_c^2$
3·26	211	487	268
2·90	220	104	156
2·54	310	2560	2380
2·16	321	3400	3173
2·01	400	2170	1750
1·74	332	2620	1603
1·65	422	3590	481
1·59	510		926
1·59	431		3264
1·48	251	0	71
1·415	440	2260	1470
1·38	530		1262
1·32	611	1580	1501
1·32	532		22
1·275	600	4980	1807
1·245	541		1961

UC_2

Uranium dicarbide had been reported as tetragonal, space group $I4/mmm$, of the calcium carbide type or an elongated fluorite structure (Litz *et al.*, 1948). The calcium carbide structure had the carbon positions along the tetragonal axis with one parameter, z, while the elongated fluorite type has fixed carbon positions at $\frac{1}{2}, 0, \frac{1}{4}$. Comparison of intensities indicated that the carbon atoms needed to be in the positions $0, 0, z$. Calculations were made with uranium atoms at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, the four carbon atoms having one parameter in position $0, 0, z$. By comparison of calculated $j|F|^2$ with those obtained from the neutron diffraction data, Table 3, the parameter z_c was found to be $0{\cdot}388\pm0{\cdot}002$, with an R factor of 0·146. Table 4 lists the interatomic distances in UC_2. The carbon atoms have the normal double-bond separation. This

Table 3. *Neutron diffraction data for* UC_2

d (Å)	hkl	$j\|F\|_o^2$	$j\|F\|_c^2$
3·03	101	0	1·5
2·98	002	10	9·1
2·53	110	76	75
1·92	112	31	36
1·77	200	131	75
1·74	103		75
1·53	211	36	3
1·52	202		36
1·496	004	6·9	1·3
1·28	114	201	5
1·25	220		75
1·24	213		149
1·16	301	313	1·5
1·15	222		36
1·14	204		5
1·13	105		138
1·12	310		151
1·04	312	166	73
1·01	303		75
1·00	006		0·5
0·960	321	206	3
0·960	224		5
0·950	215		276
0·925	116		1·7

Table 4. *Interatomic distances in uranium carbides*

	UC		
U–12 U	3·50 Å	C–12 C	3·50 Å
U–6 C	2·48		
	U_2C_3		
	for x_u = 0·050, x_c = 0·295		
U–3 U	3·34 Å	U–3 C	2·50 Å
U–2 U	3·48	U–3 C	2·56
U–6 U	3·68	U–3 C	2·82
		C–C	1·295
	UC_2		
	for z_c = 0·388		
U–8 U	3·90 Å	U–2 C	2·325 Å
U–4 U	3·54	U–8 C	2·59
		C–C	1·34

is in contrast to the thorium dicarbide monoclinic structure where the C–C distance is about 1·5 Å (Hunt & Rundle, 1950). Uranium dicarbide transforms (Wilson, 1958) at 1820 °C. to a face-centered cubic cell, 5·47 Å, of the fluorite type. This high-temperature structure of UC_2 has U–U distances of 3·88 Å, U–C distance of 2·375 Å, and C–C distance of 2·74 Å.

Discussion

The uranium carbides have strong metal–carbon bonding and weak metal–metal bonding. Rundle (1948) has proposed that monocarbides, oxides, and nitrides of sodium chloride structure exhibit resonance of hybrid *sp*-orbitals for the octahedral bonding about the non-metal atom. He indicates that such compounds are stable if the metal–metal distance expected according to Pauling's valences (Pauling, 1947) is less than the distance required for the cubic structure. For comparison, the Pauling metal radii have been calculated, allowing for the carbon double-bond character in UC_2 and U_2C_3. Table 5 lists the values together with metal radii from U–C and U–U distances. The calculated Pauling radii are close to the metal radii for U–C distances and considerably less than for U–U distances, in the case of UC and UC_2. However, U_2C_3 evidently has considerable metal–metal bonding; the shortest U–U distance corresponds to the weaker metal bonds in α-uranium. The relative weakness of the U–C bonds in U_2C_3 compared to the other carbides is also indicated by its decomposition at 1850 °C. into UC and cubic UC_2.

The bonding in UC_2 is quite similar to that in ThC_2 (Hunt & Rundle, 1950) except that the carbon–carbon bonding in UC_2 is double rather than single as in ThC_2. The increased number of valence electrons per metal atom in UC_2 compared to ThC_2 would require less electrons from carbon atoms for metal–carbon bonds, thus leaving sufficient electrons for formation of the carbon double-bond.

Table 5. *Comparison of uranium radii in carbides with Pauling radii*

Compound	r* from U–C	r from U–U	r calc.†
UC	1·71 Å	1·75 Å	1·70 Å
UC_2 tetragonal	1·65	1·77	1·70
	1·92	1·95	
UC_2 F.C.C.	1·605	1·94	1·55
U_2C_3	1·84	1·67	1·62
	1·89	1·74	
	2·15	1·84	

* r from U–C distance in tetragonal UC_2 and in U_2C_3 was taken for double bond radius of carbon.

† $r_{(1)}$ was taken as 1·45 rather than 1·42 Å given by Pauling according to later data on unit cell of body-centered γ-uranium.

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