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The Crystal Structures of UC_2*

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A high-temperature neutron diffraction study of UC_2 shows a tetragonal phase at 1700°C with the $C11a$ calcium carbide type structure, $a_0=3\cdot633$, $c_0=6\cdot036$ Å, $z=0\cdot395$, and a cubic phase at 1900°C with the $B1$ sodium chloride type structure, $a_0=5\cdot488$ Å. The cubic phase contains C_2 groups whose alignment was reduced to two possible cases, free rotation or random orientation along [111].

The phase diagram of the uranium–carbon system (Storms, 1965) lists a compound, uranium dicarbide, of approximate composition UC_2 existing in two high-temperature forms but unstable at room temperature. A structure has been described from room temperature studies of quenched samples (Litz, Garrett & Croxton, 1948; Austin, 1959) as tetragonal, space group $I4/mmm$, with uranium atoms in (0,0,0), carbon atoms in $(0,0,z)$, $z=0\cdot388$. The structure of the high temperature form has been reported from high temperature X-ray data to be the CaF_2 type (Wilson, 1960) or the FeS_2 type (Bredig, 1960).

A sample of uranium dicarbide containing excess carbon was prepared from the high-purity elements by arc-melting and pulverizing, and was examined by high-temperature neutron-diffraction (Bowman, Witteman, Arnold, Hull & Bowman, 1966). The diffraction data were obtained from $2\theta=25$ to 70° at a wavelength of 1·3926 Å, and were corrected by subtracting a blank run on the graphite sample holder. The tetragonal form was observed at 1700° and the cubic form at 1900°C. The corrected patterns are shown in Fig. 1. Observed intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to trial structures by least-squares solutions of the equation (Bacon, 1962)

$$I=K\frac{\exp\left(-\mu t\sec\theta\right)}{\sin^2 2\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2\,. \quad (1)$$

Chemical analysis of the sample showed U 90·2%, C 9·40%, free C 0·96%, O 0·15%, N 60 ppm. Accordingly, a composition of $UC_{1.85}$ was used for the intensity calculations, with scattering factors of $0\cdot85\times10^{-12}$ cm for uranium and $0\cdot661\times10^{-12}$ cm for carbon.

The tetragonal structure previously reported was confirmed, with $K=0\cdot089\pm0\cdot007$, $B=2\cdot7\pm0\cdot6$, $z=0\cdot395\pm0\cdot003$, $R=0\cdot07$, where $R=\Sigma\, w|I_o-I_c|/\Sigma\, wI_o$. Lattice parameters at 1700° were $a_0=3\cdot633$, $c_0=6\cdot036$ Å, giving a C–C distance of $1\cdot27\pm0\cdot04$ Å.

The high-temperature pattern was indexed as cubic, $a_0=5\cdot488$ Å at 1900°, in agreement with the earlier X-ray data (Wilson, 1960). The data require a sodium

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Table 1. *Neutron diffraction data for* $UC_2(t)$

d	hkl	I_o	I_c
3·11	101	<0·2	0·8
3·02	002	17·0	16·2
2·57	110	73·4	72·9
1·96	112	26·9	23·9
1·82	200	21·8	32·1
1·76	103	26·8	24·2
1·57	211	<0·2	0·3
1·56	202	13·9	13·2
1·51	004	<0·2	0·1
1·30	114	<0·2	0·3
1·28	220	12·1	12·3
1·26	213	22·0	19·4

Table 2. *Neutron diffraction data for* $UC_2(c)$

d	hkl	I_o	I_c(I)	I_c(II)
3·17	111	<0·4	0·4	0·3
2·75	200	59·4	59·6	59·6
1·94	220	29·5	26·9	27·1
1·66	311	<0·3	2·9	3·9
1·59	222	3·7	5·7	6·2
1·37	400	<0·3	1·6	0·9
1·26	331	2·6	2·3	1·9

chloride type structure containing C_2 groups similar to the structure of KCN (Elliott & Hastings, 1961; Sequeira, 1965). The absence of peaks with odd indices rules out the CaF_2-type structure and the FeS_2-type structure. The alignment of the C_2 groups was reduced to two possible cases, a free rotator model (I) with $K=0{\cdot}092\pm0{\cdot}008$, $B=7{\cdot}4\pm1{\cdot}1$, $d_{C-C}=1{\cdot}22\pm0{\cdot}11$ Å, $R=0{\cdot}056$, and a random disorder model (C_2 groups oriented along [111]) (II) with $K=0{\cdot}098\pm0{\cdot}011$, $B=7{\cdot}6\pm1{\cdot}2$, $d_{C-C}=1{\cdot}26\pm0{\cdot}15$ Å, $R=0{\cdot}065$.

The observed C–C distances, when corrected for the effect of thermal motion (Busing & Levy, 1964), fall in the range 1·32–1·40 Å, in good agreement with the value of 1·34 Å obtained at room temperature (Austin, 1959). The NaCl-type structure found for the cubic UC_2 is consistent with the observed complete solid solubility between UC (NaCl-type structure) and UC_2 at high temperatures (Storms, 1965). The marked increase in the temperature factor from the tetragonal to the cubic phase is consistent with an expected large increase in the mobility of the carbon atoms at the transition point.

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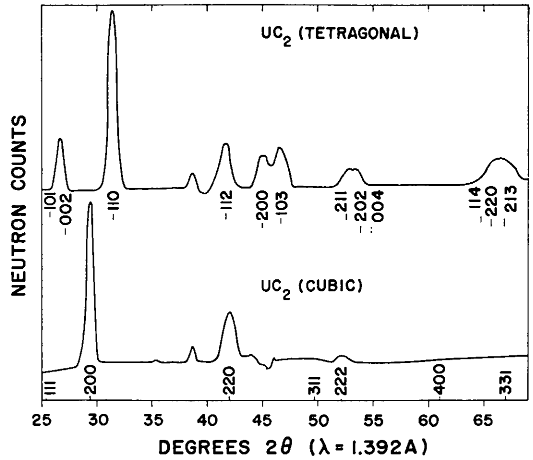

Fig. 1. Neutron diffraction powder patterns of uranium dicarbide.