Table 3. *Agreements of observed and calculated values of* $Q_{hkl} = 1/d^2_{hkl}$

	La-compound		Ce-compound		Pr-compound		Nd-compound		Sm-compound	
hkl	Q_o	Q_c	Q_o	Q_c	Q_o	Q_c	Q_o	Q_c	Q_o	Q_c
001	—	0·00263	—	0·00266	0·00289	0·00267	0·00245	0·00268	—	0·00270
010	—	0·00313	—	0·00319	0·00344	0·00317	0·00309	0·00317	—	0·00324
100	—	0·00387	—	0·00388	0·00427	0·00399	0·00411	0·00400	—	0·00398
020	0·0126	0·0125	0·0127	0·0128	0·0129	0·0127	0·0128	0·0127	0·0130	0·0130
120	—	0·0164	—	0·0166	—	0·0167	0·0166	0·0167	0·0172	0·0169
202	0·0263	0·0260	—	0·0262	—	0·0266	—	0·0267	0·0259	0·0267
131	0·0349	0·0347	0·0348	0·0353	—	0·0352	0·0349	0·0352	0·0349	0·0358
301	0·0379	0·0375	0·0380	0·0376	0·0384	0·0386	0·0388	0·0387	0·0384	0·0385
004	0·0420	0·0421	0·0425	0·0426	0·0420	0·0427	0·0425	0·0429	0·0425	0·0432
320	—	0·0473	—	0·0477	—	0·0486	0·0481	0·0487	—	0·0488
231	—	0·0483	—	0·0469	—	0·0472	0·0481	0·0472	—	0·0478
040	0·0503	0·0501	0·0512	0·0510	0·0514	0·0507	0·0512	0·0507	0·0514	0·0518
024	0·0551	0·0546	0·0556	0·0553	—	0·0554	0·0554	0·0556	0·0564	0·0562
204	—	0·0576	—	0·0581	—	0·0587	0·0592	0·0589	—	0·0591
124	—	0·0585	—	0·0586	—	0·0594	0·0592	0·0596	—	0·0614
400	0·0622	0·0620	0·0622	0·0621	0·0638	0·0638	0·0638	0·0640	0·0647	0·0637
241	—	0·0682	0·0695	0·0692	—	0·0693	—	0·0694	—	0·0705
015	—	0·0689	0·0695	0·0697	—	0·0699	—	0·0702	—	0·0707
050	—	0·0782	—	0·0798	0·0795	0·0793	0·0790	0·0792	0·0802	0·0810
341	0·0884	0·0875	0·0891	0·0886	0·0903	0·0893	0·0901	0·0894	0·0909	0·0904
432	0·1010	0·1006	0·1000	0·1014	0·1029	0·1031	0·1029	0·1033	0·1035	0·1036
305	0·1010	0·1006	0·1000	0·1014	0·1029	0·1027	0·1029	0·1030	0·1035	0·1033
060	0·1127	0·1127	0·1138	0·1148	0·1150	0·1141	0·1141	0·1141	0·1166	0·1166
054	0·1211	0·1203	0·1222	0·1223	—	0·1220	—	0·1221	—	0·1242
107	0·1316	0·1317	0·1345	0·1342	—	0·1348	—	0·1353	—	0·1363
236	0·1385	0·1383	0·1396	0·1400	0·1406	0·1406	0·1410	0·1410	0·1417	0·1423
620	0·1523	0·1518	0·1513	0·1524	0·1538	0·1563	0·1557	0·1567	0·1560	0·1562
307	0·1632	0·1637	0·1650	0·1653	0·1665	0·1667	0·1670	0·1673	0·1685	0·1681
056	0·1732	0·1729	0·1767	0·1755	—	0·1754	—	0·1757	—	0·1782
454	0·1822	0·1823	—	0·1844	—	0·1858	—	0·1861	—	0·1879
256	0·1887	0·1884	0·1895	0·1900	0·1915	0·1913	0·1920	0·1917	0·1946	0·1941
080	0·1998	0·2003	—	0·2042	—	0·2029	—	0·2029	—	0·2074
009	0·2131	0·2130	0·2149	0·2155	0·2161	0·2163	0·2167	0·2171	0·2184	0·2187
029	0·2261	0·2255	0·2276	0·2282	—	0·2289	—	0·2298	0·2272	0·2317
527	0·2394	0·2381	0·2398	0·2401	0·2434	0·2433	0·2417	0·2440	0·2451	0·2447
660	0·2523	0·2520	0·2540	0·2545	0·2574	0·2578	0·2611	0·2581	—	0·2599
149	0·2668	0·2670	—	0·2704	—	0·2710	—	0·2718	0·2704	0·2745
0,3,10	0·2912	0·2912	0·2938	0·2947	—	0·2955	—	0·2965	—	0·2991
567	0·3390	0·3383	0·3429	0·3422	0·3432	0·3447	—	0·3454	0·3444	0·3484
10,0,0	0·3875	0·3870	—	0·3880	—	0·3990	—	0·4000	0·3981	0·3980

Brazil (C. N. Pq.) they are indebted for the financial support.

References

Azaroff, L. & Buerger, M. J. (1958). *The Powder Method in X-ray Crystallography*. New York: McGraw Hill.

Ito, T. (1950). *X-ray Studies on Polymorphism*. Tokyo: Marozen.

Vicentini, G., Perrier, M. & Giesbrecht, E. (1961). *Chem. Ber.* **94**, 1153.

Acta Cryst. (1963). **16**, 322

Interatomic distances in uranium carbides.

By Brahama D. Sharma,* *Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.*

(*Received* 9 *October* 1962)

In a recent publication Austin (1959) determined the carbon positional parameters in the uranium carbides UC, U_2C_3, and UC_2 using neutron diffraction technique. In this note a treatment of the results obtained by Austin is presented which is different from that of Austin.

In his Table 5 Austin compared two sets of values of observed uranium radii in UC, U_2C_3, and UC_2 with 'Pauling radii' calculated on the basis of the well known equation of Pauling (1947) and allowing for carbon double-bond character in UC_2 and U_2C_3. One set of values corresponds to the observed (U–U)/2 distances. The second set is obtained by subtracting a carbon

---

* Present address: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

double-bond radius of 0·67 Å from U–C distances observed in U_2C_3 and UC_2, and a carbon single bond radius of 0·77 Å from U–C distance observed in UC.

The latter procedure of obtaining the radius of uranium is unjustified as one does not know the effective radius of carbon in the direction of the U–C bond without the prior knowledge of the bond order. Furthermore, the apparent assumption of a valence of 5·78 for uranium for the calculation of 'Pauling radii' can itself cause the discrepancy observed by Austin in comparing observed (U–U)/2 distances and the calculated radii.

Table 1. *Bond numbers and valences of uranium and carbon*

			Bond number n	
	Bond	Interatomic distance*	$R_1(U)=$ 1·421 Å	$R_1(U)=$ 1·45 Å
UC	C–12 C	3·51 Å	0·0005	0·0005
	C–6 U	2·48	0·33	0·37
	U–12 U	3·51	0·08	0·096
	U–6 C	2·48	0·33	0·37
$\Sigma n_{1\cdot421}$ for carbon $=1\cdot99$			$\Sigma n_{1\cdot45}$ for carbon $=2\cdot23$	
$\Sigma n_{1\cdot421}$ for uranium $=2\cdot94$			$\Sigma n_{1\cdot45}$ for uranium $=3\cdot37$	
U_2C_3	C–C	1·294 Å	2·59	2·59
	C–2 U	2·46	0·36	0·40
	C–2 U	2·59	0·22	0·24
	C–2 U	2·76	0·11	0·13
	U–3 U	3·34	0·15	0·19
	U–3 C	2·46	0·36	0·40
	U–3 C	2·59	0·22	0·24
	U–3 C	2·76	0·11	0·13
	U–6 U	3·68	0·04	0·05
	U–2 U	3·50	0·08	0·10
$\Sigma n_{1\cdot421}$ for carbon $=3\cdot97$			$\Sigma n_{1\cdot45}$ for carbon $=4\cdot13$	
$\Sigma n_{1\cdot421}$ for uranium $=2\cdot92$			$\Sigma n_{1\cdot45}$ for uranium $=3\cdot38$	
UC_2	C–C	1·34 Å	2·17	2·17
	C–U	2·320	0·61	0·68
	C–4 U	2·57	0·24	0·26
	U–4 U	3·51	0·08	0·096
	U–2 C	2·320	0·61	0·68
	U–8 C	2·57	0·24	0·26
	U–8 U	3·89	0·018	0·022
$\Sigma n_{1\cdot421}$ for carbon $=3\cdot74$			$\Sigma n_{1\cdot45}$ for carbon $=3\cdot89$	
$\Sigma n_{1\cdot421}$ for uranium $=3\cdot50$			$\Sigma n_{1\cdot45}$ for uranium $=4\cdot00$	

* These interatomic distances are calculated from the positional parameters of Austin (1959). In places they differ significantly from the values of Austin, the maximum difference being 0·06 Å for U–3 C in U_2C_3.

We here present an alternative, well known, calculation of bond numbers associated with each interatomic distance observed, and the valences of both uranium and carbon in the three carbides (Pauling, 1960). The calculations were made using two values of $R_1(U)$, namely 1·421 Å as originally suggested by Pauling (1947), and 1·45 Å as suggested by Austin (1959). The results are summarized in Table 1. The valence of uranium found by this procedure is well below the expected value of 6·0† in all the three carbides. The valence of uranium in UC and U_2C_3 is 3 and that for UC_2 is nearly 4.

An interesting observation is the valence of carbon in UC, being only 2 instead of the expected value of 4 as in U_2C_3 and UC_2. A possible explanation lies in the earlier suggestion of Rundle (1948). If one assumes carbon to have the electronic configuration,

$$1s^2,\ 2s^2,\ 2p^2$$

and by distributing the two ($2p$) electrons in the six lobes of $p(x)$, $p(y)$, and $p(z)$ orbitals, by synchronized resonance, the necessary six bonds carbon forms with uranium are achieved. This would give rise to $\frac{1}{3}$ bond character to the U–C bond, as is observed. One excess electron, the result of the valence of 3 for uranium in UC, can be visualized to be in the conduction band to explain the electrical conductivity of the carbide UC.

The observed values of valences of uranium in U_2C_3 and UC_2 can be interpreted on the lines presented by Atoji *et al.* (1958) for LaC_2 and La_2C_3. The essential feature is the formulation of these carbides as M^{+n} and C_2^{-2} groups. The excess electrons, $(n-2)$, are visualized in the conduction band with the possible sharing by the overlapping antibonding orbital of the C_2^{-2} group. The extent to which this antibonding orbital of the C_2^{-2} group partakes of the excess electrons affects the C–C bond length in the C_2^{-2} group. The correspondence of UC_2 and La_2C_3 in that the ratio of excess electrons to the number of C_2^{-2} groups is the same, namely 2, and the observed C–C bond length in the C_2^{-2} group is 1·34 Å has already been presented by Atoji *et al.* (1959). Similarly the observed C–C distances in U_2C_3 and LaC_2, 1·29 Å and 1·28 Å respectively, suggest a similar behaviour of the overlapping antibonding orbital of the C_2^{-2} group. However, the ratios of excess electrons to the number of C_2^{-2} groups are 2 and 1 for U_2C_3 and LaC_2. This would imply that U_2C_3 is a better electrical conductor compared to LaC_2.

The author is grateful to Prof. J. Donohue for introducing him to this subject, and for encouragement, and to Dr R. E. Marsh for helpful discussions. This work was supported by the National Science Foundation, U.S.A.

References

Atoji, M., Gschneidner, K., Daane, A. H., Rundle, R. E. & Spedding, F. H. (1958). *J. Amer. Chem. Soc.* **80**, 1804.

Atoji, M. & Medrud, R. C. (1959). *J. Chem. Phys.* **31**, 332.

Austin, A. E. (1959). *Acta Cryst.* **12**, 159.

Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.

Pauling, L. (1960). *The Nature of the Chemical Bond*, chapter 11. Ithaca, New York: Cornell University Press.

Rundle, R. E. (1948). *Acta Cryst.* **1**, 180.

---

† The most recent values of the valence of uranium and $R_1(U)$ are 6·0 and 1·426 Å (Pauling, 1960).