[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF THE BATTELLE MEMORIAL INSTITUTE AND THE OHIO STATE UNIVERSITY]

Preparation and Structure of the Carbides of Uranium[1]

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This paper presents data on the preparation and crystal structure of the carbides of uranium, namely, UC and UC_2. On hydrolysis, the dicarbide, UC_2, is reported to yield a mixture of gaseous, liquid, and solid hydrocarbons, a fair percentage being in the high molecular weight range.[3] This unusual fact led to a program on the investigation of the hydrolysis of heavy metal carbides, of which work this research is a part.

Preparation.—In preparing uranium carbide, previous investigators had treated U_3O_8, the "green" oxide of uranium, with graphite in an electric arc furnace. The product obtained by this method was a crystalline carbide of questionable composition containing varying amounts of impurities. In 1896, Henri Moissan,[3] who first prepared this substance, assigned it the formula U_2C_3. Later, uranium carbide was prepared by others by this method, and they assigned the formula UC_2 to the resulting compound.[4]

Because it was desirable that the carbide to be used for the hydrolysis reactions should be of high purity and definite composition, other methods of preparation were investigated. The finely divided carbide needed for the studies is pyrophoric; hence a method of preparing it in the hydrolysis apparatus was devised. The reaction between uranium metal and methane was investigated as a probable method of making the carbide with the required properties. It is known that some metals react with hydrocarbons, such as methane, below the thermal decomposition temperature of the hydrocarbons, according to the equation

$$xM + yCH_4 = M_xC_y + 2yH_2$$

It was found that finely divided uranium metal would undergo such a reaction at temperatures as low as 625°. The product of this reaction was not the dicarbide, UC_2, as had been expected, but rather a monocarbide, UC, which had not been reported previously in the literature. It has been learned since that the monocarbide, UC, was prepared and studied earlier on the Manhattan Project.[5]

The identity of the monocarbide was determined from the following experimental facts: (1) The pressure change on reaction indicated that only one mole of methane reacted per mole of uranium. (2) A molecular weight of 250 was calculated from the weight of carbide produced per unit weight of uranium metal. (3) Chemical analysis indicated the absence of free carbon and confirmed the formula UC. (4) X-Ray diffraction studies showed that, to the limit of detection, metallic uranium and free graphite were absent. (5) A single phase having a face-centered cubic structure was indicated for the monocarbide; the dicarbide, UC_2, is tetragonal.

The apparatus in which the reaction between methane and uranium metal was carried out is illustrated in Fig. 1. It is designed so that the hydrolysis studies may also be carried out following the preparation of the carbide. The basic parts are the "Vycor" furnace tube, surrounded by an electrical resistance furnace; vacuum pumps capable of evacuating the system to a pressure of 10^{-5} mm. of mercury; a McLeod gage and mercury manometers for pressure measurement; a Toepler pump which is used to transfer gases from one part of the system to another; reservoirs for purified hydrogen and methane; and, a constant-volume buret. Advantage is taken of the ease of formation and decomposition of uranium hydride, as determined by F. H. Driggs,[6] to convert the uranium metal into a very finely divided form. A weighed quantity of metal is placed in a platinum boat in the furnace tube and the system is evacuated. Hydrogen is then admitted and allowed to react with the metal at 225°, where the equilibrium pressure of the hydride is about 3 mm. When all of the metal has been converted to hydride, the temperature is raised to 450°, where the equilibrium pressure is greater than 700 mm., and the hydride is caused to decompose by keeping the pressure in the system below this value. This cycle is repeated three times, after which the hydrogen is pumped off, the temperature increased to the desired reaction temperature, and a measured quantity of methane is added. The reaction is allowed to proceed until equilibrium is reached, after which the gaseous products are withdrawn for analysis and a second charge of methane is added. This process is continued until no further reaction is observed. When a fixed quantity of methane is added each time, the resulting equilibrium pressure of methane and hydrogen, at a fixed temperature, is dependent on the substances present in the solid phase. Thus, the equilibrium pressure over a mixture of uranium and uranium monocarbide is higher than that over a mixture of uranium monocarbide and uranium dicarbide. By plotting the equilibrium pressure against the per cent. of carbon in the solid phase, as determined by the amount of methane which has reacted, vertical breaks in the curve will be obtained

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(1) (a) Presented before the Inorganic and Physical Chemistry Division of the American Chemical Society at the Chicago meeting, 1946; (b) this material is to be included as part of the thesis to be presented by Lawrence M. Litz to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

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(3) H. Moissan, *Ann. chim. phys.*, [7] **9**, 302 (1896).

(4) P. Lebeau, *Compt. rend.*, **152**, 955 (1911); O. Ruff, *Z. anorg. Chem.*, **72**, 65 (1911).

(5) Pending publication of the Manhattan District's work in this field, the following statement is made at the suggestion of Dr. F. H. Spedding, Project Director of the Atomic Research Institute, Ames, Iowa: "The monocarbide, UC, was discovered on the Manhattan Project at the Iowa State College at Ames in 1942 through X-ray diffraction. The lattice and structure were determined by R. Rundle, and the chemical identity was established by V. H. Carter and A. D. Tevebaugh. The U-C phase diagram was carefully studied in the UC range by Carter, A. H. Daane, Rundle, and A. I. Snow. These studies will be published when released." This information was, however, unknown to the present authors until after the completion of the studies reported in this paper.

(6) U. S. Patent 1,816,830 (1929).

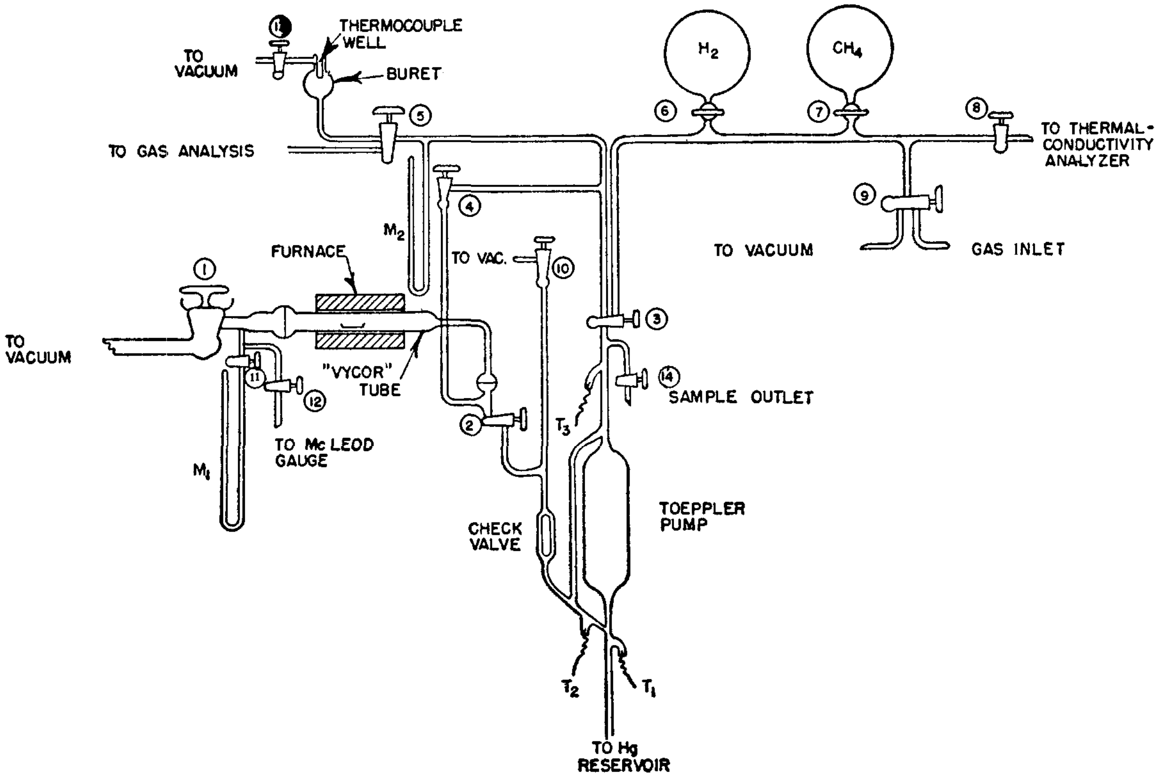

Fig. 1.—Vacuum apparatus for the investigation of the uranium metal–methane reaction.

which will indicate phase changes. In the case of uranium, no lower carbides than the monocarbide were observed, and the rate of reaction between the methane and the monocarbide at temperatures up to 900° was too slow to allow investigation of higher carbide phases.

Other methods of preparing both these carbides were investigated. The following equations indicate the reactions which were successfully used

(1) $U + C = UC$ (2100°)
(2) $U + 2C = UC_2$ (2400°)
(3) $U_3O_8 + 11C = 3UC + 8CO$ (1800°)
(4) $U_3O_8 + 14C = 3UC_2 + 8CO$ (2400°)

By treating uranium metal with graphite at 2100°, well-defined metallic crystals of the monocarbide were produced. By increasing the reaction temperature to approximately 2400°, the dicarbide was obtained. The preparation of the monocarbide by reaction of the U_3O_8 with graphite is accomplished easily by heating a powdered mixture of the two, of stoichiometric proportions, as indicated by equation (3), to 1800°, a sintered, coke-like mass being produced by this means. Higher temperatures are again required to prepare pure UC_2, for if the mixture, made up according to the indicated equation, is heated to temperatures below 2400°, the proportion of UC_2 in the product decreases as lower temperatures are used. At 2400°, the dicarbide is formed as large crystalline masses by this latter process. Both the monocarbide and the dicarbide form crystals which are hard and brittle and metallic in appearance. In neither case were these large enough for single crystal X-ray studies.

Because the preparation of the dicarbide, UC_2, made necessary the use of very high temperatures, the furnace assembly (Fig. 2) was employed. H is a 30-turn, water-cooled, copper induction coil which was activated by a 60KVA Ajax high-frequency converter. The graphite crucible A was heated inductively and it, in turn, heated the graphite crucible B, which carried the reactants, by radiation. Temperatures were measured through the hole in the lid by means of a Leeds and Northrup optical pyrometer. Heat loss was prevented by the lampblack insulation J, and excessive burning at the top was inhibited by the sillimanite cover D. Because of the arrangement at the top of the crucible A, influx of air into the reacting system was at a minimum, and there was no noticeable oxidation of the crucibles B and C, or of the product.

X-Ray Measurements.—The X-ray diffraction patterns were recorded both photographically and by a motor-driven spectrometer synchronized with a Brown recording potentiometer. The crystal lattice constants were determined with a Debye–Scherrer cylindrical camera of 37.8-mm. radius using Cu-Kα radiation. A suspension of the fine powder in Canada balsam was painted on a hair which was then mounted on the geometric axis of the camera in a fixture which rotated it during the exposure. Quantitative intensity measurements were made on an X-ray spectrometer using a Geiger tube as the detector. This can be connected either to a standard scaling circuit or to an integrating circuit connected to the potentiometer.

For accurate work, the motor drive and potentiometer were cut out of the system and the quantity of radiation per unit-time interval was counted at manually set positions of the detector. To obtain the intensity, the number of counts was plotted as a function of angle and the area under the curve determined, the intensity being proportional to the area. To insure total reflection of the incident beam, the sample employed was made of a thick block of the finely ground carbide, sieved to pass 325-mesh screen. Considerable difficulty was encountered with these compacts because of what appeared to be orientation of the particles. In the case of the monocarbide, this was evidenced by a very large increase in intensity of the (200) line relative to the (111) line, the former being approximately twice as strong as the latter in the most extreme case encountered. As is seen in Table I, the calculated values are in the reverse order. By suspending the sample in paraffin wax or by using a carbide of very small crystal size, as is prepared by reaction of very finely divided uranium metal with methane, this effect may be eliminated.

Because of the arrangement of the X-ray tube in the spectrometer, only those lines obtained by diffraction through a Bragg angle less than 45° can be measured. Therefore, for those lines appearing in the back-reflection direction, only estimated intensity values, obtained from the Debye–Scherrer films, could be determined. Also, in the case of the dicarbide, many of the lines were too close together for adequate resolution, and only four of the relatively important lines were measured and these are listed in Table II. Relative intensities were determined in all cases.

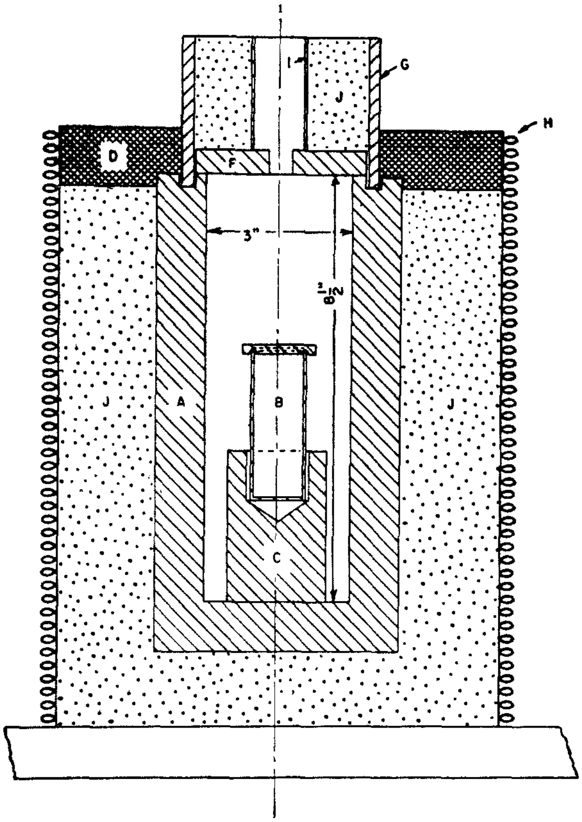

Fig. 2.—High-temperature induction furnace for preparation of uranium carbides.

Table I

Comparison of Observed Spacings and Intensities with Calculated Values for Two Possible Uranium Monocarbide Structures

Spacings calculated using $a_0 = 4.955$ Å. Intensities calculated relative to the (111) line for the sodium chloride and zinc blende types of structures. Observed intensities obtained spectrometrically and photographically. Visual estimates of line intensities on photographic film: VS = very strong, S = strong, MS = moderately strong, M = medium, W = weak, and VW = very weak.

hkl	*d*, calcd.	*d*, obsd.	*I/I* (111) calcd. NaCl	*I/I* (111) calcd. ZnS	*I* estd. photog.	*I/I* (111) obsd. spect.
111	2.861	2.868	1.000	1.000	VS	1.00
200	2.477	2.477	0.600	0.470	S	0.62
220	1.752	1.752	.430	.394	MS	.44
311	1.494	1.496	.444	.435	S	.44
222	1.430	1.433	.148	.118	W	.16
400	1.239	1.240	.058	.054	VW	.05
331	1.137	1.138	.175	.169	M	.19
420	1.108	1.110	.179	.150	M+	.19
422	1.011	1.012	.157	.144	M	——
333	0.954	0.954	.048	.046	M	——
511	.954		.143	.140		
440	.876	.877	.100	.092	W	——
531	.838	.837	.409	.402	S	——
600	.826	.826	.061	.049	MS	——
442	.826		.245	.196		
620	.783	.783	.485	.444	S	——

Table II

Comparison of Observed Spacings and Intensities with Calculated Values for Two Possible Uranium Dicarbide Structures

Calculated spacings for $a_0 = 3.54$ Å., $c_0 = 5.99$ Å. Intensities calculated relative to the (101) line for the calcium carbide structure with $z = {}^3/_8$, and for the elongated calcium fluoride type of structure. Observed intensities obtained spectrometrically and photographically. Visual estimates of line intensities on photographic film: VS = very strong, S = strong, M = medium, W = weak, VW = very weak, VVW = very, very weak.

hkl	*d*, calcd.	*d*, obsd.	*I/I* (101) calcd. CaC_2	*I/I* (101) calcd. CaF_2 elong.	*I* estd. photog.	*I/I* (112) × 0.31 obsd. spect.
101	3.046	3.040	1.000	1.000	VS	——
002	2.981	2.982	0.262	0.199	M	——
110	2.503	2.496	.397	.262	S	0.40
112	1.920	1.919	.310	.310	S	.31
200	1.770	1.771	.140	.123	M	.17
103	1.737	1.739	.254	.203	S	.24
211	1.531	1.527	.268	.258	S	——
202	1.523		.147	.113		
004	1.496	1.497	.029	.033	VW	——
114	1.284	1.285	.072	.063	W	——
220	1.251	1.253	.039	.034	VW	——
213	1.240	1.241	.137	.113	M	——
301	1.158	1.156	.050	.049	W	——
222	1.154		.055	.044		
204	1.142	1.145	.046	.053	W	——
105	1.133	1.134	.057	.045	W	——
310	1.119	1.118	.053	.035	W	——
312	1.048	1.047	.088	.087	M	——
303	1.015	1.016	.047	.037	VW	——
006	0.997	1.001	.011	.008	VVW	——
321	.969	0.969	.085	.082	M	——
224	.960	.960	.040	.047	VW	——
215	.955	.956	.100	.082	M	——
116	.926	.928	.046	.046	W	——
314	.896	.896	.081	.071	W	——
400	.885	.881	.030	.026	M	——
323	.881		.116	.093		
206	.869	.871	.054	.042	W	——
411	.850	.849	.107	.103	M	——
402	.849		.059	.047		
305	.840	.841	.068	.055	M	——
330	.834	.832	.039	.026	M	——
107	.831		.061	.059		
332	.804	.803	.082	.082	W	——
420	.792	.791	.106	.106	M	——
413	.788	.788	.246	.196	S	——

Crystal Structure of Uranium Monocarbide.—The diffraction pattern obtained by the Debye-Scherrer method indicated that uranium monocarbide is face-centered cubic with $a_0 = 4.955$ Å. The observed spacings and intensities are given in Table I. In deciding on the positions of the carbon atoms, one is faced with two possibilities. If the carbon atoms occupy the octahedral interstices in the lattice formed by the uranium atoms, the sodium chloride structure is obtained, as in Fig. 3a; whereas, if the alternate tetrahedral holes are filled, the zinc blende structure, Fig. 3b, is obtained. The space groups and the equivalent points for the two structures are

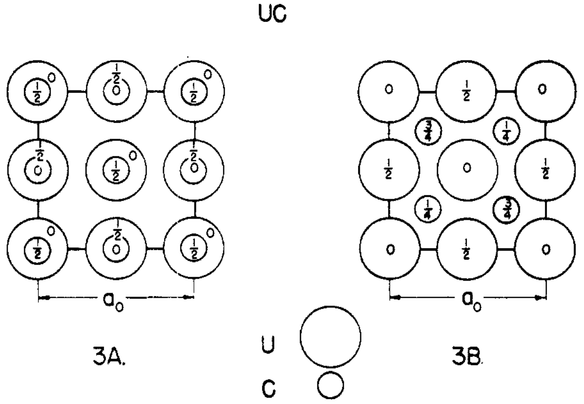

Fig. 3.—A, Sodium chloride structure; B, zinc sulfide structure.

Sodium chloride structure $O_h^5 - Fm3m$
$(0,0,0;\ 0,{}^1/_2,{}^1/_2;\ {}^1/_2,0,{}^1/_2;\ {}^1/_2,{}^1/_2,0) +$
U 4(a) 0,0,0
C 4(b) $^1/_2,{}^1/_2,{}^1/_2$

Zinc blende structure $T_d^2 - F\bar{4}3m$
$(0,0,0;\ 0,{}^1/_2,{}^1/_2;\ {}^1/_2,0,{}^1/_2;\ {}^1/_2,{}^1/_2,0) +$
U 4(a) 0,0,0
C 4(c) $^1/_4,{}^1/_4,{}^1/_4$

The calculated values of Table I are the intensities relative to the (111) line for each of the structures. The relation

$$I \propto pF^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

was used to obtain the calculated intensities. p is a multiplicity factor, F, the crystal structure factor, and the trigonometric function of the Bragg angle, θ, contains the Lorentz and polarization factor and a geometric factor entering because of the experimental method. The intensity of the diffracted radiation from both the thin sample on the hair and the thick block of powdered material is given by this formula. Because the necessary data were not available, the structure factor was not corrected for temperature effect. Only the constant of proportionality is different for the two methods, and this is not of interest in the calculation of relative intensities. All of the required quantities were obtained from the "Internationale Tabellen."[7]

By comparing the measured intensities, as obtained on the X-ray spectrometer, with those calculated for the two possible structures, it was found that satisfactory agreement is obtained with the sodium chloride structure. The relative magnitude of the first two lines is particularly significant. The Debye–Scherrer films also support the sodium chloride structure in that it is observed that the (420) line is of slightly greater intensity than the (331) line. The calculations indicate the reverse to be true for the zinc blende structure. The proximity of these two lines on the photographic film permits rather accurate estimates of their relative intensity—a fact suggested to the authors by R. Rundle, who determined the structure of this compound for the Manhattan District project.

Crystal Structure of Uranium Dicarbide.—The dicarbide is reported in the literature to have a tetragonal structure with $c/a = 1.7$ for the body-centered tetragonal cell,[8] in agreement with the observations of the authors. However, the lattice constants are not given and in order to obtain them it was necessary to index the lines. This was accomplished with the aid of a Davey chart for body-centered tetragonal lattices. The values obtained were $a_0 = 3.54$ Å., $c_0 = 5.99$ Å. The observed spacings and those calculated from these values of the lattice constants are given in Table II. It has been noticed that when the dicarbide contains some monocarbide, as the result of incomplete conversion, a noticeable decrease in the lattice spacing occurs, particularly in the direction of a_0.

The problem of determining the positions of the carbon atoms in uranium dicarbide is somewhat more complicated than in the monocarbide. The

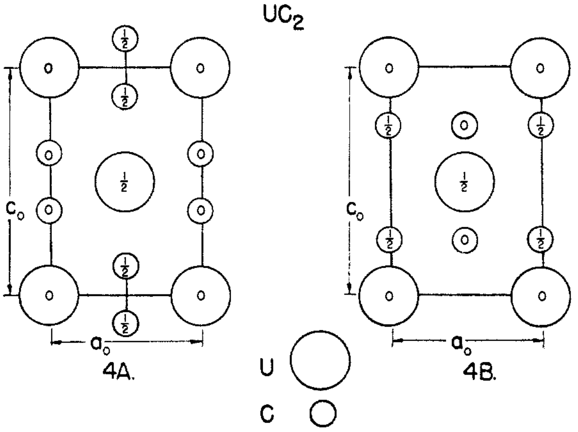

Fig. 4.—A, Calcium carbide structure; B, elongated fluorite structure.

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(7) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," 2 Band, 1935.

(8) *Strukturber.*, **2**, 276 (1928-1932); G. Hagg, *Z. physik. Chem.*, **B 12**, 42 (1931).

two structures which might be obtained by adding another carbon atom to the structures considered for the monocarbide are indicated in Fig. 4. By placing two carbon atoms in each of the octahedral interstices in the uranium lattice in a manner so that the carbon–carbon axis are parallel to one edge of the unit cell, one obtains the calcium carbide structure indicated in Fig. 4a. This was the structure assigned to uranium dicarbide by Hagg, presumably because the axial ratio is the same as that of calcium carbide. In the other structure, derived from the zinc blende structure, each carbon atom is at the center of a deformed tetrahedron, as in Fig. 4b. This is similar to the fluorite structure with tetragonal deformation. The space groups and equivalent points for these two structures are given below

Calcium carbide structure
D_{4h}^{17} (0,0,0; $^1/_2,^1/_2,^1/_2$) +
U 2(*a*) 0,0,0
C 4(*e*) 0,0,*z*; 0,0$\bar{z}$

Elongated fluorite structure
D_{4h}^{17} (0,0,0; $^1/_2,^1/_2,^1/_2$) +
U 2(*a*) 0,0,0
C 4(*d*) $^1/_2$,0,$^1/_4$; 0,$^1/_2$,$^1/_4$

Intensity calculations made for several values of the carbon-to-carbon distance of the two adjacent carbon atoms in the calcium carbide structure showed variations too small in magnitude to aid in deciding the correct distance. The values in the fifth column of Table II are for $z = 3/8$, which corresponds to a carbon-to-carbon distance of 1.50 Å., slightly less than the single bond distance.

The observed intensities are seen to be in best agreement with the calcium carbide structure. Points of significance are the relative intensities of the (110) and (112) lines and the (204) and (105) lines, where the calculated intensity gradient is in the opposite sense for the two structures. In both cases, the observed values are in the direction predicted by the calcium carbide structure. Because of the low resolving power of the spectrometer, adjacent lines overlap in several instances and, for this reason, only the (110), (112), (200), and (103) lines were measured spectrometrically. The general trend of values obtained from the spectrometer is in agreement with the estimated order of intensities obtained from the photographic method.

Discussion.—Before the completion of the experimental work on the determination of the positions of the carbon atoms, the problem had been approached using the concept of atomic radii. Calculations applying this method had indicated that the structures arrived at later experimentally were the less likely. In the case of both the monocarbide and the dicarbide, the uranium radii required to provide atom-to-atom contact in Structures 3A and 4A were decidedly greater than those existing in the metal and, since the radii of a metal usually decrease on compound formation, these structures had appeared unlikely. With the zinc blende and elongated fluorite structures, Figs. 3B and 4B, the required uranium radii agreed very well with metallic radii for uranium. The evidence obtained from the X-ray diffraction studies appears rather strong in the other direction, and it would seem that these materials represent an anomaly in the theory of atomic radii. The pronounced orientation effect observed with the monocarbide also supports the conclusion that its structure is that of sodium chloride, as the strengthening of the (200) line indicates cleavage along the cube faces. Since cleavage usually occurs along planes of highest density of atoms, and this is the (100) plane in the sodium chloride and the (111) plane in the zincblende structure, the former is preferred.

Information gathered in the study of the hydrolysis of these carbides may help to clarify this apparent anomaly.

Summary

Uranium dicarbide, UC_2, and the previously unreported monocarbide, UC, have been prepared by several methods. The crystal lattice constants have been determined for the two structures, and X-ray diffraction evidence is presented which indicates that the monocarbide has the sodium chloride type of structure, and the dicarbide has the calcium carbide type of structure.

The lattice constants observed are: UC, a_0 = 4.995 Å.; UC_2, a_0 = 3.54 Å.; c_0 = 5.99 Å.

COLUMBUS, OHIO RECEIVED JUNE 23, 1947