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THE ATOMIC STRUCTURE OF CARBORUNDUM DETERMINED
BY X-RAYS.

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Introduction.

The more perfect specimens of carborundum, as prepared from carbon and silica in the electric furnace, usually consist of hexagonal crystal plates with well-developed (111) faces together with minor prisms and pyramids. Because of the extraordinarily close crystallographic relationships between carborundum (ditrigonal pyramidal class) and diamond (cubic-tetrahedral class) and their closely related physical properties, it may be expected that the two substances will be somewhat similar in their atomic structures. It is through the precise study of similarly constituted compounds that a knowledge of the chemical and physical forces acting on the atoms will be obtained and for this reason the determination of the atomic structure of carborundum is of importance.

The research was begun in the laboratory of Professor W. H. Bragg in the University of London and was continued at the Massachusetts Institute of Technology with the aid of a grant made to Dr. A. A. Noyes by the Carnegie Institution of Washington. To Professor Bragg and Dr. Noyes the authors wish to render acknowledgment for their having facilitated in every way the progress of the research.

Description of Apparatus and Procedure.

Three types of equipment for X-ray excitation were tested, namely, the induction coil with mercury break, the open core interrupterless transformer, and the closed core interrupterless transformer. The measurements with the X-ray spectrometer show there are no characteristic differences between these different sources of excitation. For the accurate measurements transformer excitation was employed, the time of closure of the primary circuit being governed by an automatic switch directly connected to a synchronous motor. By this procedure a definite reproducible number of waves or pulses are sent through the X-ray tube delivering, therefore, a certain constant quantity of electrical energy to the tube.

The X-ray spectrometer was similar to that described by W. H. and W. L. Bragg.¹ The X-ray tube used in conjunction with the spectrometer was provided with a target of pure palladium metal.

Two crystals were used in the investigation, the first being a specimen of the ordinary steel-blue product and the second a light green transparent hexagonal plate. This latter crystal was selected from a number loaned for the investigation by Dr. C. H. Warren of the Massachusetts Institute of Technology. Although so different in color there is otherwise little difference between the two varieties, the interplanar distances being in all cases the same for corresponding faces and the relative intensities of reflection differing not more greatly in crystals of the two types than in various individuals of the same type. The difficulty of securing a crystal of carborundum free from twinning and crystalline intergrowths is due in large measure to the rapidity of growth, the irregularity of position and the unevenness of the temperature during formation.

Except for the basal plane (111), the reflections from the crystal planes were measured irrespective of whether the faces corresponding to these planes were developed. The reflection angles and intensities from the following planes were determined. For convenience both Miller and Bravais indices are given.

Miller.	Bravais.		
111	= 0001	111	= 02 $\bar{2}$ 1
100	= 01 $\bar{1}$ 1	2 $\bar{1}\bar{1}$	= 10 $\bar{1}$ 0
1 $\bar{1}$ 0	= 11 $\bar{2}$ 0	11 $\bar{3}$	= 40 $\bar{4}$ 1
		41 $\bar{2}$	= 11 $\bar{2}$ 1
		52 $\bar{1}$	= 11 $\bar{2}$ 2

In the (11 $\bar{3}$) and (77 $\bar{5}$) positions reflections at approximately one-half the theoretical angle and one-sixth the theoretical angle were found. These reflections were produced by growths upon these planes of plates showing the (111) face. In fact, in one instance recurring (111) reflections were obtained on one side of the (1 $\bar{1}$ 0) face at the angles 2° 10', 4° 5', 9° 35', 13° 35', 19° 20', 26° 35', and 27° 35' and at 0° 41',

¹ "X-Rays and Crystal Structure," 1915, p. 22.

$6^{\circ} 15'$, $10^{\circ} 50'$, $15^{\circ} 55'$, $19^{\circ} 25'$ (I11), $21^{\circ} 5'$, $25^{\circ} 25'$, and $26^{\circ} 40'$ on the other. There is no regularity in the occurrence of these planes and the phenomenon is to be explained by the fact that the carborundum during its rapid growth becomes a rather disordered and unhomogeneous structure.

The brilliance and sharpness of the reflections from a carborundum crystal are shown by Fig. 1. It was possible to trace the reflections from the basal face (I11) around to a chamber angle of 89° , that is, to the sixth order spectrum. The stray radiation in the case of carborundum was always small in amount and it was found that the ratios of intensi-

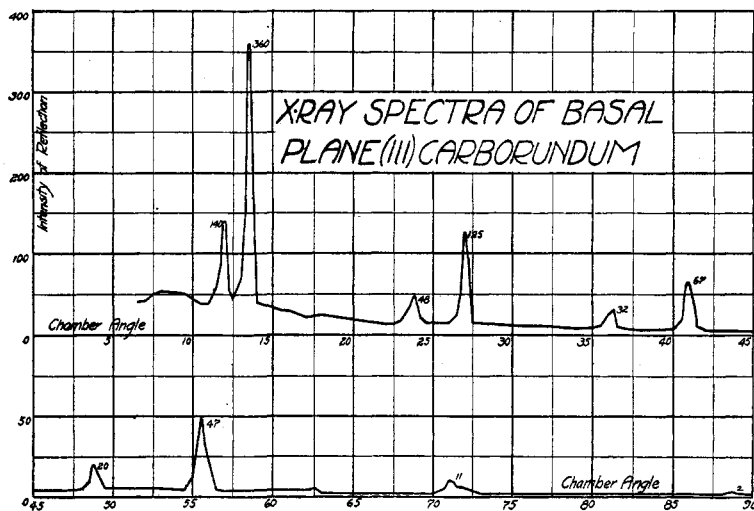


Fig. 1.

ties of reflection for the different orders remained practically unchanged whether this stray radiation was included or not. For the reflections from the (I11) face of the crystal, the ratios, making no correction for stray radiation, were 100 : 35 : 19 : 13 and after making the correction 100 : 34 : 19 : 13.

In determining the angles corresponding to maximum intensity of reflection, the opening of the chamber aperture was kept at 1.0 mm. and in determining the relative intensities of reflection the chamber aperture was 2.0 mm. The aperture of the slit (commonly called Slit "B") controlling the width of X-ray beam striking the crystal was for the intensity measurements kept at the width of 3.0 mm.

Since imperfections in crystals may be responsible for irregularities in the observed intensities of reflection, conditions of measurement should be chosen so that the influence of these irregularities may be minimized. For this reason the total area from which reflections take place should be

TABLE I.—SUMMARY OF OBSERVED AND CALCULATED RESULTS.

Crystal plane.	Order of reflection.	Crystal I. Chamber angle.		Crystal II. Chamber angle.		Angle of reflection.			Electroscope deflection.		Ratio intensity.		
		Obs.	Corr. ¹	Obs.	Corr.	Obs. I.	Obs. II.	Calc.	Obs. I.	Obs. II.	Obs. I.	Obs. II.	Calc.
111 = 0001....	I	13° 30'	13° 20'	13° 30'	13° 20'	6° 40'	6° 40'	6° 40'	360	430	100	100	100
	II	27° —	26° 50'	27° —	26° 50'	13° 25'	13° 25'	13° 25'	125	238	35	55	31
	III	40° 55'	40° 45'	40° 45'	40° 35'	20° 23'	20° 18'	20° 23'	67	165	19	38	19
	IV	55° 30'	55° 20'	55° 15'	55° 05'	27° 40'	27° 33'	27° 40'	48	100	13	23	4
	V	71° 00'	70° 50'	35° 25'	...	35° 29'	11	...	3	...	2
	VI	88° 45'	88° 35'	44° 18'	...	44° 9'	2.5	...	1	...	2
x = 0.36													
100 = 0111....	I	15° 40'	15° 42'	15° 30'	15° 24'	7° 51'	7° 42'	7° 42'	35	12	100	100	100
	II	31° 40'	31° 42'	31° 12'	31° 6'	15° 51'	15° 33'	15° 32'	44	55	126	470	72
	III	47° 30'	47° 32'	47° 30'	47° 24'	23° 46'	23° 42'	23° 41'	20	23	57	196	17
	IV
x = 0.42													
110 = 1120....	I	21° 35'	22° 03'	21° 20'	21° 58'	11° 02'	10° 59'	10° 55'	67	97	100	100	100
	II	44° 32'	45° —	44° 10'	44° 48'	22° 30'	22° 24'	22° 15'	41	37	61	38	20
	III	69° 30'	69° 58'	69° —	69° 38'	34° 59'	34° 49'	34° 36'	15	7	22	7	7
	IV
x = 0.0													

$11\bar{1} = 02\bar{2}1 \dots$	I	$13^{\circ} 25'$	$13^{\circ} 19'$	$13^{\circ} 25'$	$13^{\circ} 03'$	$6^{\circ} 40'$	$6^{\circ} 32'$	$6^{\circ} 39'$	103	140	100	100	$x = 0.21$
	II	$26^{\circ} 57'$	$26^{\circ} 51'$	$26^{\circ} 40'$	$26^{\circ} 18'$	$13^{\circ} 26'$	$13^{\circ} 9'$	$13^{\circ} 24'$	36	52	35	37	100
	III	$40^{\circ} 50'$	$40^{\circ} 44'$	$40^{\circ} 40'$	$40^{\circ} 18'$	$20^{\circ} 22'$	$20^{\circ} 9'$	$20^{\circ} 21'$	45	80	44	57	7
	IV	$55^{\circ} 25'$	$55^{\circ} 19'$	$54^{\circ} 40'$	$54^{\circ} 18'$	$27^{\circ} 40'$	$27^{\circ} 9'$	$27^{\circ} 38'$	18	20	18	14	5
$2\bar{1}\bar{1} = 10\bar{1}0 \dots$	I	$38^{\circ} 35'$	$38^{\circ} 19'$	$38^{\circ} 22'$	$38^{\circ} 22'$	$19^{\circ} 10'$	$19^{\circ} 11'$	$19^{\circ} 8'$	78	52	100	100	$x = 0$
	II	$82^{\circ} 20'$	$82^{\circ} 04'$	$82^{\circ} 10'$	$82^{\circ} 10'$	$41^{\circ} 02'$	$41^{\circ} 05'$	$40^{\circ} 59'$	17	14	23	27	20
	III
$11\bar{3} = 40\bar{4}1 \dots$	I	$25^{\circ} 45'$	$25^{\circ} 21'$	$25^{\circ} 20'$	$25^{\circ} 41'$	$12^{\circ} 41'$	$12^{\circ} 51'$	$12^{\circ} 51'$	70	83	100	100	$x = 0.12$
	II	$52^{\circ} 30'$	$52^{\circ} 06'$	$52^{\circ} 25'$	$52^{\circ} 46'$	$26^{\circ} 03'$	$26^{\circ} 23'$	$26^{\circ} 26'$	9	10	12	12	14
	III
$41\bar{2} = 11\bar{2}1 \dots$	I	$25^{\circ} 45'$	$25^{\circ} 47'$	$25^{\circ} 25'$	$25^{\circ} 38'$	$12^{\circ} 54'$	$12^{\circ} 49'$	$12^{\circ} 50'$	33	91	100	100	$x = 0.36$
	II	53°—	$53^{\circ} 2'$	$52^{\circ} 30'$	$52^{\circ} 43'$	$26^{\circ} 31'$	$26^{\circ} 22'$	$26^{\circ} 22'$	7	19	21	21	31
	III	84°—	$84^{\circ} 13'$...	$42^{\circ} 07'$	$41^{\circ} 46'$...	7	...	8	19
$52\bar{1} = 11\bar{2}2 \dots$	I	$34^{\circ} 30'$	$35^{\circ} 02'$	35°—	$35^{\circ} 28'$	$17^{\circ} 31'$	$17^{\circ} 44'$	$17^{\circ} 26'$	58	75	100	100	$x = 0.28$
	II	$73^{\circ} 30'$	$74^{\circ} 02'$	$74^{\circ} 35'$	$75^{\circ} 03'$	$37^{\circ} 01'$	$37^{\circ} 32'$	$36^{\circ} 48'$	6	8	10	11	13
	III

¹ The corrected chamber angles were calculated according to the method described by Burdick and Ellis, THIS JOURNAL, 39, 2520 (1917).

kept nearly constant. If the X-ray beam is wide enough to cover the whole face of the crystal, then the areas of the atom planes producing the reflection are constant for the different orders and accidental irregularities are largely eliminated. It may be shown that for a perfect crystal the intensity ratios of reflection for the different orders should be unaffected by variation in the width of the beam. A small angular rotation of the crystal causes a shift only in the spot on the crystal surface from which the reflections take place and both the intensities and the chamber angles remain practically unaffected. With a wide beam the reflection is from the most perfect portion of the face, that is, the part in which the regularity of structure is best preserved.

Summary of the Observations.

Table I summarizes the observations on two different crystals, Crystal I being steel-blue in color and Crystal II being pale green and transparent.

Interpretation of Results.

The angle between the edges of the elementary rhombohedron of carborundum is $89^{\circ} 56.6'$ and the hexagonal axis ratio $a : c$ is 1.2265 according to the crystallographic measurements of Negri.¹ For an isometric crystal the angle between the edges of the rhombohedron is 90° and the hexagonal axis ratio is 1.2248. The elementary rhombohedron of carborundum thus departs from the simple cube only by an amount equal to 0.15% shortening or contraction along the hexagonal axis. For approximate purposes it is certainly admissible to consider the carborundum crystal to be cubic in form.

For the three types of cubic lattices, known as the cube, the face centered cube, and the cube centered lattice, the interplanar distances in the directions normal to the three fundamental planes (100), (110), and (111), are $1 : 0.707 : 0.573$, $1 : 0.707 : 1.146$ and $1.414 : 0.573$. The distance between the like planes of atoms, according to the law of X-ray reflection, is inversely proportional to the sines of the angles of reflection for the X-rays. The values of the above ratios for the carborundum lattice are

$$\frac{1}{\sin 7^{\circ} 42'} : \frac{1}{\sin 10^{\circ} 59'} : \frac{1}{\sin 6^{\circ} 40'} \quad \text{or}$$

$1 : 0.702 : 1.152$. These ratios show that the fundamental lattice of the carborundum structure is of the face centered type.

Since the heavy atoms of the structure determine the character of the lattice and, therefore, the angles at which reflection of the X-rays may occur, it is obvious that the silicon atoms, which are the relatively heavier atoms in carborundum, constitute this face centered lattice. The close agreement between the observed and calculated angles of reflection

¹ Negri, *Rivista d. min. e crist. ital. Pad.*, 29, 33 (1903); *Z. Krystall.*, 41, 269 (1904); also Groth, *Chemische Kristallographie*, 1, p. 56.

for all planes shown in Table I furnishes fundamental proof that the correct type of lattice has been selected.

The position of the carbon atoms in this structure of silicon is determined by consideration of the intensity ratios. There are three possible ways in which it may be conceived that the carbon atoms may be fitted in, satisfying the condition that carbon and silicon atoms occur in equal numbers and that the symmetry of the structure shall not be of a lower order than that required crystallographically. These are shown in Figs. 2, *a*, *b* and *c* as projections along the hexagonal axes.

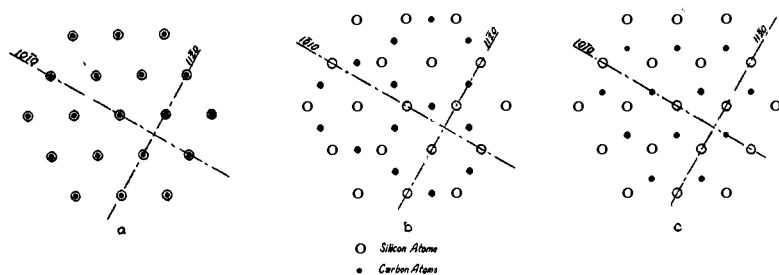


Fig. 2.

The relative intensity ratios for the different orders of reflections from the prism faces $(11\bar{2}0)$ and $(10\bar{1}0)$ have approximately the normal values indicating that the carbon atoms lie in the planes of the silicon atoms and that they are not displaced by one-third or one-half the interplanar distances as the diagrams *b* and *c* require. When reference is made to a model it is quickly seen also that the atoms are neither to be disposed so as to explain the intensities of reflection from the other faces (notably the (100) face) nor can they be placed in positions which will yield a stable structure. The possibility of the *b* or *c* arrangement is then eliminated.

From a consideration of the intensities of reflection from the (100) faces the approximate position of the carbon atoms may be fixed quite independently of any other data. Since the intensity of reflection for the second order relative to the intensity for the first order was found to be greatly increased over that which would be expected were the spacing of the planes the normal one it is inferred that the planes of carbon atoms are not far from midway between the (100) planes of silicon atoms. In order to satisfy this condition and to conform to the crystallographic requirements of symmetry, the carbon atoms must be located on a face centered lattice similar to the silicon lattice and displaced with respect to it by a certain distance along the hexagonal axis of the rhombohedron. The normal reflections given by the $(11\bar{2}0)$ and $(10\bar{1}0)$ faces furnish corroborative evidence that the carbon atoms lie along the rhombohedral axis immediately beneath the silicon atoms, as indicated in Fig. 2, *a*.

If the displacement of the carbon planes with respect to the silicon planes for the (100) faces were exactly one-half the interplanar distance the carborundum crystal would have almost the exact structure of the diamond, except for the very slight distortion along the hexagonal axis. It should therefore be determined if the experimental data are in accord with this middle position for the carbon atoms. Half spacing for the (100) faces requires that in a direction perpendicular to the (111) faces the relative displacement must be one-quarter of the interplanar distance. For dissimilar planes whose interplanar displacement is one-quarter, it is readily to be shown that the first and third order reflections will be approximately in normal ratio to one another. For the second order, however, the intensity of the reflection will be strongly diminished, since there is complete opposition of phase in the two superimposed wave trains; and for the fourth order, since there is exact phase register, the reflection will be strongly increased. The ratio of the intensity of the second order reflection to the fourth order reflection may, therefore, be regarded as a sensitive criterion for indicating the closeness of approximation to quarter spacing. Calculations based on the theory that the intensity of reflection is proportional to the square of the mass per unit area, show that if the displacement of the carbon planes is one-quarter of the interplanar distance between (111) silicon planes, the relative intensities of the first four orders of reflection would be 100 : 6 : 7 : 7. The expected ratio of intensities for the second and fourth would thus be 1 : 1.2 whereas the observed value of the ratios was 35 : 13 or 1 : 0.4. It is clearly seen that the second order reflection is not weak enough, and the fourth order reflection is not strong enough to satisfy the condition of quarter spacing.

The exact determination of the relation of the carbon lattice to that of the silicon atoms can only be made by the general method of analysis. The algebraic expression¹ for the resultant intensity I_n of a reflection of the n th order is $I_n = K_n (M_1^2 + M_2^2 + 2M_1M_2 \cos 2\pi nx)$ in which M_1 and M_2 represent the mass per unit area in the primary and secondary atom planes, x the fractional displacement of the total interplanar distance of the primary and secondary atom planes, and K_n the series of constants which have the values of 100, 20, 7 and 4 for the reflections of the first, second, third and fourth orders, respectively. From this general expression for the spectrum intensity may be calculated the values of the relative intensities for the different orders of reflection for all values of the fractional displacement x . The theoretical variation of the intensities of reflection for alternating planes of silicon atoms and planes of carbon atoms for all possible values of x are shown in Fig. 3.

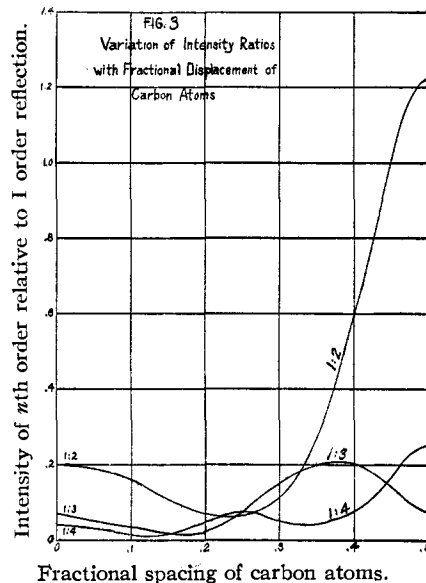
In comparing the observed spectra intensities with the calculated, it is

¹ Burdick and Ellis, *THIS JOURNAL*, 39, 2524 (1917).

seen that, since the observed intensity of reflection for the third order from the (111) face is not stronger than the second order reflection, the lower limit for the relative spacing of the (111) planes of the carbon and silicon lattice is fixed to be not less than 0.33. Since the second order reflection from the (111) planes is not more than one-half as intense as the first order reflection, the upper limit for the fractional displacement may be placed at about 0.4. The fact that the third order is relatively strong with respect both to the second and fourth orders also leads one to limit the upper value of the fractional spacing at about 0.4.

In order to avoid ambiguity of meaning when referring to other planes in the crystal, let these lower and upper limits of spacing be designated as the **A** and **B** arrangements of atoms. The **A** spacing (which was 0.33 for the (111) planes) gives, according to the geometrical requirements of the lattice, a spacing of 0.44 for the (100) planes and the **B** spacing (which was 0.40 for the (111) planes) gives 0.40 for the (100) plane spacing. The reflections from the (100) planes, in which the observed intensity of the second order was much stronger than the intensity of the first, show that the 0.4 spacing necessary in the **B** arrangement of atoms is certainly low which, contrariwise, indicates that the corresponding spacing for the (111) planes (0.4) was estimated at too high a value. The **A** spacing of 0.33 is reasonable for any higher value of x would produce for the (111) planes only a slight increase in the value of the second order intensity of the (100) reflection.

Study with the aid of a model shows that the relative position of the carbon lattice with respect to the silicon lattice is between the limits represented by the **A** and **B** arrangements. The mean value of the fractional displacement of the carbon atoms along the hexagonal axis is thus approximately 0.36 ± 0.03 . The complete structure of the carborundum crystal is represented in Fig. 4. The calculated values of the intensities tabulated in the last column of Table I have been made using the value of 0.36 for the displacement of the two lattices. Close agreement between calculated and observed



values cannot be expected as was explained earlier. There is, however, approximate accordance.

As a final test of the correctness of the structure he rededuced for carborundum its density may be calculated. Associated with each point of

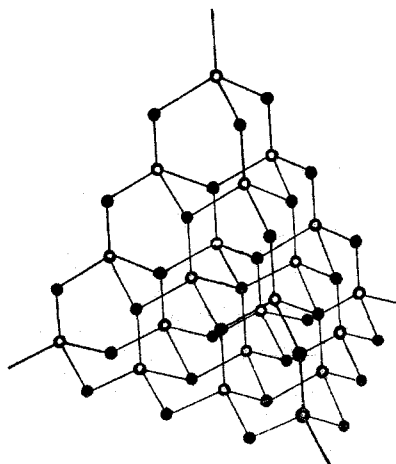


Fig. 4.

structure, which is equivalent to one atom groups CSi, there are two elementary rhombohedra having edges equal to the 100 spacing of the planes. The angle of reflection for the palladium rays ($\lambda = 0.504 \times 10^{-8}$ cm.)¹ from the 100 face of carborundum is $7^\circ 42'$ and the interplanar distance calculated by the formula $d = \lambda/2 \sin \theta$ is 2.179×10^{-8} cm. The volume of the two elementary rhombohedra is 20.70×10^{-24} cc. Since the weight of the hydrogen atom is 1.64×10^{-24} g., the weight of the atom group CSi is $28.3 + 12.0/1.008 \times 1.64 \times 10^{-24}$ or 65.5×10^{-24} g. The

calculated density is then $65.5/20.7$ or 3.11 , which compares favorably with the value of 3.123 obtained by Richards.²

The carborundum structure thus shows itself to be very similar to the tetrahedral diamond lattice, each being constituted by two intersecting face centered lattices. The difference in symmetry of the two structures is explained by the relative shift of the two systems of lattices with respect to one another. In the case of the diamond, the amount of shift along the cube diagonal is exactly 0.5 of the elementary diagonal length or 0.75 of the (111) interplanar distance, whereas in the case of carborundum the shift is 0.42 of the rhombohedron diagonal or 0.64 of the (111) interplanar distance.

In accounting for this displacement on the basis of atom structure it seems that the forces of attraction along the rhombohedral axis of the lattices are greater than are exerted in the other directions. This may be interpreted to mean that the forces of attraction along the axis of a silicon atom are greater than about the periphery. This property manifests itself by the contraction along the tetrahedral axis of the crystal, and by the displacement of the silicon atoms (or carbon atoms, it being immaterial which lattice is under consideration) toward the apices of the surrounding tetrahedra. Calculations on the basis of a unit tetrahedron show that in order to secure stability of a structure in which the center

¹ Kaye, "X-Rays," 1917, p. 226.

² Richards, *J. Franklin Inst.*, 136, 287 (1893).

atom is not at the center of gravity of the tetrahedron but is 0.36 of the altitude above the base, the attraction in the axial direction must be 1.37 times greater than in the direction of the bonds to the other immediately adjacent atoms. In a complete structure of indefinite extension, such as a crystal approximates, this value of the axial attraction ratio will be somewhat greater than 1.37.

Summary.

Measurements of the angles of reflection of palladium X-rays from the principal planes of a crystal of carborundum and measurements of the intensities of reflection of the different orders have been made and interpreted. The results show that the silicon atoms and carbon atoms in carborundum are each arranged on face centered rhombohedral lattices, very nearly cubic ($\alpha = 89^\circ 56.6'$) displaced with respect to one another along the hexagonal axis a distance equal to 0.36 of the basal plane (111) spacing.

The elementary tetrahedron of carborundum is, therefore, very similar to that of the diamond, the difference consisting in a slight shortening of the vertical axis (0.15%) and a displacement of the atoms of carbon from the centers of the tetrahedron (0.25 of the altitude in the case of the diamond) to a position slightly less distant from the apex (0.36 of the altitude in the case of carborundum).

From the values of the distances between the atom planes as derived from the X-ray measurements the density of carborundum was calculated to be 3.11 whereas the observed value is 3.123.

SHEFFIELD, ALA.

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

VOLUMETRIC DETERMINATION OF REDUCING SUGARS. A SIMPLIFICATION OF SCALES' METHOD FOR TITRATING THE REDUCED COPPER WITHOUT REMOVING IT FROM THE RESIDUAL COPPER SOLUTION.

BY W. BLAIR CLARK,¹
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One who contributes to the now voluminous literature of reducing sugar determinations must show a good excuse for his temerity. Especially is this so in view of such exhaustive investigations as have been conducted in recent years by Benedict,² Kendall³ and Peters,⁴ to cite

¹ Biochemist, cotton, truck and forage crop disease investigations, U. S. Department of Agriculture.

² Stanley R. Benedict, "The Detection and Estimation of Reducing Sugars," *J. Biol. Chem.*, **3**, 101-117 (1907); "A Method for the Estimation of Reducing Sugars," *Ibid.*, **9**, 57-59 (1911).

³ E. C. Kendall, "A New Method for the Determination of the Reducing Sugars," *THIS JOURNAL*, **34**, 317-341 (1912).

⁴ Amos W. Peters, "Sources of Error and the Electrolytic Standardization of the