in chemisorption to a large extent even at cracking temperatures.

It might be pointed out in connection with these results that physical adsorption of normal paraffins could be important in the decomposition of much higher hydrocarbons in this series. At temperatures of 450°, paraffins from $C_{16}$ to $C_{20}$ have a relative pressure of about 0.01 to 0.05, at which upwards of a monolayer of physical adsorption might be expected to form.

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[CONTRIBUTIONS FROM THE UNIVERSITY OF MISSOURI, SCHOOL OF MINES AND METALLURGY, DEPARTMENT OF METALLURGY]

# Precision Determination of Lattice Parameter, Coefficient of Thermal Expansion and Atomic Weight of Carbon in Diamond[1]

BY M. E. STRAUMANIS AND E. Z. AKA

Four diamond samples from the Belgian Congo were used for the investigation. Spectrographic analysis revealed the presence of traces of fifteen elements in the samples. The lattice parameter determinations were carried out by means of the asymmetric method, with a 64 mm. precision camera in a thermostat at five constant temperatures (10, 20, 30, 40 and 50°). The powder mounts, 0.12 mm. in diameter, were translated and rotated during the exposure in order to assure uniformity of the lines. Only the (331)-Co$K\beta_1$ line was used for the determinations. The three clear white diamond samples showed the same lattice parameter; 3.55960 ± 0.000016kX. (3.56679 Å.) at 20°, corrected for refraction. The accuracy of determination was better than 1:200,000. The parameter of gray boart was 3.55968 ± 0.00003kX. at 20°. The thermal lattice expansion coefficient, as determined from all samples, was $(1.38 \pm 0.12) \times 10^{-6}$. The atomic weight of carbon in the clear diamond samples was 12.0096 (the average value of the densities obtained by Bearden and Tu being used for the calculations). This weight is 0.003% lower than the chemical atomic weight, but is well within the error limit of the method. Therefore, the diamond lattice is sound and the method of lattice constant determination applied is an absolute one. Comparison with the work of other authors shows that clear white diamonds usually have the same lattice constants as noted above. Thus, the impurities are included mechanically. However, a very limited formation of a solid solution with silicon or other elements is not excluded (gray boart).

## Introduction

The greatest accuracy previously attained in the determination of the lattice parameters of diamond (±0.00005 Å.), was achieved by Lonsdale[2] and Tu.[19] As the asymmetric method[3a,b] allows still greater precision, the determinations were repeated with four kinds of diamond (white boart, gray boart, and two diamond stones of gem quality—No. 1 and No. 2, all from the Belgian Congo) at closely controlled temperature intervals. The thermal lattice expansion coefficient thus determined, together with the computed atomic weight of carbon in diamond, provide data for the discussion of the soundness of diamond crystals,[4] the solubility of solids in diamonds frequently found in these stones,[5] and the applicability of diamond powder as a standard substance for Debye–Scherrer photographs.[6]

## Spectroscopic Analysis and Experimental Procedure

Diamonds No. 1 and 2 were irregular octahedrons, containing microscopic inclusions and weighing 0.118 and 0.17 g., respectively. After the stones had been crushed in a steel mortar, the powder was treated with hot hydrochloric acid in order to remove any iron.

Semi-quantitative analyses of three diamond samples based on emission spectra (arc method),[7,8] were carried out with an Abney grating spectrograph having a range capable of detecting the elements usually found in diamonds.[5] All precautions were taken to detect all of the trace elements and to introduce no new ones. Only a visual examination of the relative line intensities was made (Table I).

TABLE I

IMPURITIES IN THE DIAMOND SAMPLES

Abbreviations: xxxx—major contamination; xxx—strong trace; xx—trace; x—faint trace; ?—questionable

| Impurity | Gray boart | Diam. No. 1 | Diam. No. 2[a] |
|---|---|---|---|
| Al | xxx | xxx | xxx |
| B | x | x | .. |
| Ca | xxx | x | xxxx |
| Co | .. | xx | .. |
| Hf | xxx | .. | x |
| Fe | xxx | ? | x |
| Pb | .. | ? | ? |
| Mg | xxxx | xxxx | xx |
| Mn | x | .. | ? |
| Pt | .. | .. | x |
| Si | xxx | xxxx | xx |
| Ag | xx | .. | xx |
| Sn | xx | .. | .. |
| Ti | x | xx | xxx |
| Zn | .. | xx | .. |

[a] The sample was treated with HF for 12 hours in a Pt crucible.

Among the 15 elements found, magnesium, aluminum, silicon, calcium, and titanium constitute a persistent group which appeared in all three diamond samples. The relative concentrations of silicon and aluminum agreed with the ob-

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(1) Based on a thesis submitted by E. Z. Aka to the Graduate School of the University of Missouri, School of Mines and Metallurgy, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the 1950 Spring Meeting of the American Crystallographic Association in Penn. State College.

(2) K. Lonsdale, *Phil. Trans. Roy. Soc. (London)*, **A240**, 219 (1946).

(3) (a) M. E. Straumanis, *J. Appl. Phys.*, **20**, 726 (1949); (b) M. Straumanis and A. Ievins, "Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode," J. Springer, Berlin, 1940; reprinted by Edwards Brothers, Inc., Ann Arbor, Michigan, 1948.

(4) M. E. Straumanis, *Acta Crystallogr.*, **2**, 82 (1949).

(5) C. F. Chesley, *Am. Mineral.*, **27**, 27 (1942).

(6) W. Trzebiatowski, *Roczniki Chem.*, **17**, 73 (1937).

(7) R. A. Sawyer, "Experimental Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1944, p. 298.

(8) G. R. Harrison, R. C. Lord and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 428.

servations of Chesley.[5] The treatment of diamond powder No. 2 with hydrofluoric acid (7 $N$) and subsequent washing did not remove the silicon from the sample.

The exact value of the lattice parameter of diamond was determined at ten degree intervals between 10 and 50°, using the following equipment: (1) a precise 64 mm. powder camera, (2) a jacket into which the camera fitted and in which a constant temperature (±0.02°) could be maintained by a circulating bath system, and (3) a comparator accurate to 0.001 mm. for measuring the films 18 cm. in length.[3] Bare films could be inserted into the camera in the asymmetric position; this arrangement permits the computation of the exact Bragg angles without knowledge of the camera radius, without the use of a standard substance, and without any corrections for film shrinkage.

The diamond powder was sieved through silk bolting cloth (approximately 320 mesh) and the powder mounts, 0.12 mm. in diameter, were made from the finer material. Thus, the mounts were thin enough and sufficiently transparent to X-rays so that the absorption correction could be neglected.[3a,b] The sharpest and most uniform lines were obtained when the mounts were almost perfectly centered by means of the sample holder, which was rotated and simultaneously scanned over a range of 3 mm. in the inside of the camera. The 6-cm. long pinholes (collimators) had a bore of 0.5 or 0.8 mm. The lines were measured from peak to peak intensity. The patterns were indexed by a graphical method.[9]

With cobalt radiation under the angle $\vartheta \cong 82°$, diamond powders yielded the $(331)K\beta_1$-line, which developed intensely enough in 1.5 to 2 hours of exposure to allow accurate lattice parameter determinations. In order that the factors of conversion (from mm. to degrees),[3] might be calculated two sets of lines in the front reflection region were also measured. At each temperature three films were made, and the simple average of the parameters computed was chosen as a final value. The wave length for $\text{Co}K\beta_1 = 1.61744$ kX. (Siegbahn) was used.

## The Lattice Parameter and Expansion Coefficient of Diamond

The purpose of Table II is to show (1) the values of the lattice parameters obtained at different temperatures, (2) the variations in the values at one constant temperature, and (3) the method of attack. $\varphi$ is the back reflection angle.

TABLE II

VARIATION OF LATTICE PARAMETERS OF DIAMOND NO. 1 WITH TEMPERATURE

| Temp., °C. | $\varphi$, degrees | Parameter, kX. | Aver. param., kX. |
|---|---|---|---|
| 10 | 7.964 | 3.55945 | |
| | 7.976 | 56 | 3.55950 |
| | 7.968 | 50 | |
| 20 | 7.974 | 3.55954 | |
| | 7.994 | 72 | 3.55953 |
| | 7.948 | 32 | |
| 30 | 7.984 | 3.55963 | |
| | 7.976 | 56 | 3.55959 |
| | 7.978 | 58 | |
| 40 | 7.991 | 3.55969 | |
| | 7.981 | 60 | 3.55965 |
| | 7.988 | 66 | |
| 50 | 7.994 | 3.55972 | |
| | 7.998 | 75 | 3.55971 |
| | 7.989 | 67 | |

Since diamond has the smallest expansion coefficient of any of the elements,[10] the interval of 10° was too small; some of the measurements, therefore, overlap. The worst fluctuations of lattice constants, not observed on other films with other samples, were recorded at 20°. These fluctuations may have been due to the non-uniform shrinkage of films. Nevertheless, the average values of the table show a definite increase of lattice constants with temperature. So the non-uniform shrinkage errors were nearly nullified by the use of several films.

The measurements with the other three kinds of diamonds were carried out exactly in the same way as already shown (Table III).

TABLE III

VARIATION OF LATTICE PARAMETERS OF 4 KINDS OF DIAMOND WITH TEMPERATURE

| Sample | Average lattice parameter in kX. at 10° | 20° | 30° | 40° | 50° |
|---|---|---|---|---|---|
| White boart | 3.55951 | 3.55955 | 3.55956 | 3.55964 | 3.55970 |
| (Gray boart | 61 | 61 | 65 | 70 | 81) |
| Diam. No. 1 | 50 | 53 | 59 | 65 | 71 |
| Diam. No. 2 | 51 | 59 | 59 | 64 | 71 |
| Average | 3.55951 | 3.55956 | 3.55958 | 3.55964 | 3.55971 |

Except for the case of gray boart, the lattice constants agree very well at all temperatures. Therefore, the average was taken without the data for the gray boart.

The lattice expansion coefficient $\alpha$ can be computed from the formula

$$\alpha = \frac{a_{t_2} - a_{t_1}}{a_{t_1}(t_2 - t_1)} = \frac{\Delta a}{a\Delta t} \tag{1}$$

where $a_{t_1}$ and $a_{t_2}$ are the lattice constants at $t_1$° and $t_2$°, respectively. The coefficient was determined for all possible combinations between $a_{t_1}$ and $a_{t_2}$,[11] on the assumption that the coefficient does not change appreciably in the small interval of 40° (Table IV).

TABLE IV

THERMAL LINEAR LATTICE EXPANSION COEFFICIENT OF DIAMOND SAMPLES BETWEEN 10 AND 50°

| Sample | $\alpha \times 10^6$ |
|---|---|
| White boart | 1.32 |
| Gray boart | 1.38 |
| Diamond No. 1 | 1.51 |
| Diamond No. 2 | 1.29 |
| Average | $(1.38 \pm 0.12) \times 10^{-6}$ |

The fluctuations of the $\alpha$-values are caused by experimental errors, and there seems to be no connection between these fluctuations and the impurities present in the samples. The value $1.38 \times 10^{-6}$ agrees fairly well with the common coefficient obtained by Fizeau for 20, 40 and 50°: 0.89, 1.18 and $1.32 \times 10^{-6}$.[12]

Table V shows the data of Table III reduced to 20° (equation 1), and indicates the reproducibility of the measurements.

The correction for refraction was introduced by means of Ewald's formula.[13] The parameters of white clear diamond at 18 and 25° are 3.55959 kX. (3.56678 Å.) and 3.55962 kX. (3.56681 Å.), respectively.

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[9] M. Straumanis, *Z. Krist.*, **104**, 167 (1942).

[10] M. E. Straumanis, *J. Appl. Phys.*, **21**, 936 (1950).

[11] M. Straumanis and A. Ievins, *Z. anorg. Chem.*, **238**, 175 (1938).

[12] Fizeau, *Compt. rend.*, **68**, 1125 (1869).

[13] W. Wien and F. Harms, "Handb. der Experimentalphysik," XXIV/2, pp. 94, 116; see also F. Foote, *J. Chem. Phys.*, **3**, 605 (1935).

TABLE V

LATTICE PARAMETERS OF WHITE DIAMOND SAMPLES AND GRAY BOART REDUCED TO 20°

(See Table III); $\alpha = 1.38 \times 10^{-6}$

| Temp., °C. | Lattice parameters at 20° of White diamond | Gray boart |
|---|---|---|
| 10 | 3.55956 | 3.55966 |
| 20 | 6 | 1 |
| 30 | 3 | 0 |
| 40 | 4 | 0 |
| 50 | 6 | 6 |
| Average = | 3.55955 | 3.55963 |
| Refraction: | 5 | 5 |
| | 3.55960<br>±0.000016 | 3.55968<br>±0.00003 kX. |
| or | 3.56679 Å. | |

The length of the single C—C bond in diamond is 1.54135 kX. or 1.54447 Å. at 20°.

## Atomic Weight of Carbon

The high reproducibility obtained does not yield any information as to the systematic error involved in these measurements. The absolute accuracy of the lattice constant determination of an element can be tested by calculating its atomic weight from the values of the lattice parameter and the density, and by comparing the resulting atomic weight with the chemical atomic weight of the element. Such determinations of high accuracy were first made by Hutchinson and Johnston.[14]

The atomic weight $A_x$ of carbon in diamond was calculated in a different way in the present paper, in that Avogadro's number was used[15]

$$A_x = kN_svd/n \qquad (2)$$

$v$ is the volume of the unit cell (in kX.$^3$), $d$—the density (g./cm.$^3$), $n$—the number of atoms per unit cell, $N_s$—Siegbahn's Avogadro number,[16] and $k$ is a constant factor equal to 1.0002.[15,17]

The relative error by which the atomic weights from X-ray and density data are affected, can be calculated from formula (3), which is derived by logarithmic differentiation of equation 2, and elimination of $v$

$$\Delta A_x/A_x = 3\Delta a/a + \Delta k/k + \Delta d/d \qquad (3)$$

$N_s$ and $n$ are constants.

The densities of diamond were taken from the papers of Bearden[18] and Tu.[19] The following data were obtained for the atomic weight of carbon in diamond.

TABLE VI

ATOMIC WEIGHT OF C, CALCULATED FROM X-RAY (TABLE V) AND DENSITY DATA OBTAINED WITH PUREST DIAMOND

| Author | $d$ of diamond in g./cm.$^3$ | Temp., °C. | $A_x$ of C | $A_{\text{chem.}}$ of C | $A_x - A_{\text{chem.}}$ | Δ, in % |
|---|---|---|---|---|---|---|
| Bearden | 3.51536 | 23.5 | 12.0117 | 12.010 | +0.0017 | +0.014 |
| Tu | 3.5142 | 18 | 12.0075 | 12.010 | − .0025 | − .02 |
| Average | | | 12.0096 | 12.010 | − .0004 | − .003 |

Assuming that the density measurements of both Bearden and Tu are excellent, the simple average might be expected to give the best value. The atomic weight obtained, as compared with the internationally accepted chemical value, was too low by only 0.0004. This deviation is completely within the error limits of the method applied, because it follows from equation (3) for the limit

$$\Delta A_x = 8.35 \times 10^{-5} \times 12 = \pm 0.001 \qquad (4)$$

It was assumed that $3\Delta a/a = 3 \times 4.5 \times 10^{-6}$; $\Delta k/k = 5 \times 10^{-5}$ and $\Delta d/d = 2 \times 10^{-5}$. The accuracy of this method of atomic weight determination is, of course, lower than that of the chemical method, because the error involved by the chemical method ($\Delta k/k = 5 \times 10^{-5}$) is already implied in equation 4. If the wave lengths are expressed in Å., an uncertainty of at least the same magnitude is included in $N_0$.

## Discussion

On the assumption (1) that the method of lattice constant determination using the asymmetric film arrangement is absolute (no standard substances are necessary); and, (2) that the correction factor $k$ in equation 2 is justified, the data of Table VI prove that the diamond crystals used are sound (within the error limits there are no vacant sites and no interstitial atoms).[15] The correctness of the two assumptions has already been shown by previous work.[8,15] It may seem unlikely that a precision of better than 1:200,000 could be attained in a small 64 mm. camera (Table V, white diamond). However, it was recently shown by Keith that the 64 mm. camera with asymmetric film arrangement worked as precisely as a large 190 mm. Unicam camera.[20]

Comparison of the average lattice constant for white, clear diamond (Table V) with those obtained by other authors[2] revealed that the values just determined are nearly or completely within the error limits given by the previous authors, except for some measurements by the single crystal method where the diamond crystals were probably distorted (the powder method is not affected by this disadvantage). Hence, the minor impurities found in diamond samples are not dissolved, but mechanically included. However, the possibility of a very slight solubility of silicon or other elements in diamond is not excluded. In these cases the lattice constant may increase by 0.00008 kX. (Table V). This possibility also might explain the differences in densities of diamond crystals,[18] if the presence of rough inclusions is excluded. Nevertheless, diamond powder of good quality can be used as a standard substance.[6] In this respect diamond is more reliable than quartz[21]; on the other hand, it has the disadvantage that diamond produces only a few lines on the films. In view of

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(14) C. A. Hutchison and H. L. Johnston, THIS JOURNAL, **62**, 3165 (1940); **63**, 1580 (1941); C. A. Hutchinson, *J. Chem. Phys.*, **10**, 489 (1942); D, A. Hutchinson, *ibid.*, **13**, 383 (1945).

(15) M. E. Straumanis, *Acta Crystallogr.*, **2**, 82 (1949); *Z. Physik*, **126**, 49 (1949).

(16) M. Siegbahn, "Spektrosckopie der Röntgenstrahlen," 2. Aufl., J. Springer, Berlin, 1931, p. 43.

(17) M. Straumanis, *Z. Physik*, **126**, 62 (1949).

(18) J. A. Bearden, *Phys. Rev.*, **54**, 698, 700 (1938).

(19) Y. Tu, *ibid.*, **40**, 662 (1932).

(20) H. D. Keith, *Proc. Phys.* (*London*), **B63**, 1034 (1950).

(21) H. D. Keith, *ibid.*, **B63**, 208 (1950).

this fact it is best not to use standard substances at all, but to apply the method used here.

**Acknowledgment.**—The authors wish to express their sincere appreciation to Professor A. Legsdin, Department of Metallurgical Engineering and Mineral Dressing of the Missouri School of Mines and Metallurgy, for his coöperation in carrying out spectrographic analyses of the diamond samples.

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[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY, GENERAL ELECTRIC COMPANY]

# Thorium Complexes with Chloride, Fluoride, Nitrate, Phosphate and Sulfate[1]

BY E. L. ZEBROSKI, H. W. ALTER AND F. K. HEUMANN

The dependence of the thorium extraction equilibrium on the fourth power of TTA activity and the minus fourth power of hydrogen ion activity was demonstrated, confirming that Th(IV) is a simple (hydrated) tetrapositive ion in perchlorate solutions of acidity greater than about 0.08 *M*. The association constants for the first several complexes of thorium ion with fluoride, chloride, nitrate, sulfate and phosphate ions, respectively, have been determined in acid media by the TTA distribution method. Evidence was obtained that complexes like $Th(H_2PO_4)^{+++}$, $Th(H_2PO_4)_2^{++}$ and $Th(SO_4)_2$ are measurably weak acids in 1 to 2 molar acid solutions.

## Thorium Ion Complex Equilibria

Of the tetravalent ions thorium ion is of particular interest in complexing studies because of its large ionic radius relatively simple electronic configuration, and the absence, in acid solutions, of the complicating effects of hydrolysis and polymerization. Its complexing properties have been rarely studied until recently, however, because many of the usual methods of measurement of complex ion equilibria are inapplicable to most thorium complexes, particularly when the complexing ion or molecule is present in excess.

The method used here has been applied by Connick and Reas[2] and Connick and McVey to the investigation of the complexing and hydrolytic behavior of zirconium.

## Experimental

**Experimental.**—The distribution measurements were performed using a solution of thenoyltrifluoracetone,[3] which for convenience is called TTA, in benzene as extractant for thorium. The aqueous phases contained thorium ion at a concentration of 3 to 5 × $10^{-4}$ *M*, from 0.0875 to 2.00 *M* perchloric acid, and added salts as indicated. The solutions were maintained at constant ionic strength, $\mu$, with sodium or lithium perchlorate.

The two liquid phases were contacted at 25.0 ± 0.1° by shaking in glass stoppered vessels or by mechanical stirring in small long-necked flasks fitted with close fitting teflon or fluorothene bearing sleeves to prevent evaporation. Preliminary experiments showed that the extraction equilibrium with respect to thorium was probably diffusion limited with a half-time of the order of 0.1 minute, but since equilibrium with respect to TTA distribution is slow the phases were agitated for a period of 30 minutes or longer. Aliquot parts were withdrawn from both phases by micropipet. Results are given as a distribution coefficient $R$ = (thorium in organic phase)/(thorium in aqueous phase) based on the average of duplicate or quadruplicate analyses of both phases. The thorium activity from either phase was then transferred to 8 *N* $HNO_3$ by appropriate semi-microextractions and re-extractions with 1 *M* TTA in benzene and 8 *N* $HNO_3$, respectively. The resulting nitric acid solution was evaporated on one-inch platinum discs and the alpha activity counted with a methane proportional counter. In the individual extractions the total concentration of Th(IV) in aqueous phases (before extraction) averaged about 3 × $10^{-4}$ *M*.

**Materials.**—Vacuum distilled TTA was obtained from Prof. M. Calvin of the University of California Radiation Laboratory; it was used without further purification. Stock solutions were made up in thiophene-free benzene and stored in glass vessels covered with aluminum foil to exclude light.

Sodium and lithium perchlorates obtained from the G. Frederick Smith Company were recrystallized before use. The major impurity from a complexing standpoint was sulfate. Since this was not completely removed by recrystallization, barium sulfate was precipitated from the reagents during purification, except in the study of nitrate and sulfate complexing. About $10^{-3}$ *M* $Ba(ClO_4)_2$ was present in other extraction experiments.

Sodium nitrate, sodium chloride and sodium sulfate were recrystallized reagent grade salts. The perchloric acid was the triple distilled G. F. Smith product.

The tracer was $Th^{230}$ (ionium) which emits 4.68 mev. alpha particles with a half-life of 80,000 years. It was obtained from the Argonne National Laboratory in dilute nitric acid solution. It contained about six times as much by weight of $Th^{232}$.

**Treatment of Distribution Data.**—For purposes of calculation the data are treated as though the activity coefficients of all species in solution remain strictly constant at constant ionic strength. The association constants are expressed as concentration equilibrium constants and are strictly valid only for solutions of the compositions of a given experiment.

The reactions of thorium in acid solution with an anion whose electrical charge is $-x$ may be written

$$Th^{+4} + nX^{-x} = ThX_n^{+4-nx} \qquad (1)$$

the general equilibrium constant is

$$K_n = (ThX_n^{+4-nx})/(Th^{+4})(X^{-x})^n \qquad (2)$$

From material balance

$$(Th_t) = (Th^{+4})\left(1 + \sum_n K_n(X^{-x})^n\right) \qquad (3)$$

where $(Th_t)$ is the total metal ion concentration in an aqueous phase and $n$ covers the range of the number of ligands considered.

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[1] Presented at the 119th Meeting of the American Chemical Society, April 11, 1951, Cleveland, Ohio. The method employed here and examples of its application to nitrate, sulfate and phosphate complexes was described in a paper by E. L. Zebroski and F. K. Heumann and presented at an A. E. C. Information Meeting, Chicago, Ill., October 19, 1948. This work was carried out under the auspices of the Atomic Energy Commission.

[2] R. E. Connick and W. Reas, AECD-2491; R. E. Connick and W. McVey, THIS JOURNAL, **71**, 3181 (1949).

[3] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).