

The only conclusion which can be drawn from the preceding paragraph is that the low-density Bose gas near $T=0$ does not exist when $a_s < 0$. That is to say, a Bose gas having short-range interactions with $a_s < 0$ will collapse to densities such that the low-density approximations (10) and (10') are not valid. For a Bose gas with weak long-range attractions, the calculation of Huang¹¹ has shown that the low-density approximations (10) and (10') may remain valid in certain circumstances even though $a_s < 0$. To show this, Huang considers a nonlocal, or velocity-dependent, two-particle

interaction, which is equivalent in this case to considering a very-low-momentum variation of $g_{i,j}$ in the approximation (89).

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Silicon-Crystal Determination of the Absolute Scale of X-Ray Wavelengths*†

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In a recent evaluation of the atomic constants, the value of Avogadro's number is $N = 6.02252 \times 10^{23}$ (g mole)⁻¹ ± 11 ppm (probable error). Measurements on the atomic weight of silicon give $A = 28.0857 \pm 10$ ppm. Precision measurements of the density of silicon combined with the above values in the Bragg equation $a = (fA/\rho N)^{1/3}$ result in an absolute grating constant of high precision. X-ray diffraction measurements with the same crystal yield the grating constant in x units; thus the conversion factor from x units to cm can be evaluated. X-ray and density measurements have been made on 17 selected silicon crystals from four different sources. The statistical error in the measurement of the densities of the 17 crystals was ± 0.4 ppm. To obtain the absolute density error, a 3 ppm probable error in the density of water must be added, giving a total error of ± 3.1 ppm. The measured densities of two of the 17 crystals differed from the average by more than 3σ , probably indicating a difference in the density of the crystals. The x-ray diffraction measurements were made with a double-crystal spectrometer using the copper $K\alpha_1$ and $K\alpha_2$ lines. The wavelengths in angstroms were evaluated from the Bragg law for each of the 17 crystals and for the α_1 and α_2 lines. The average wavelengths were Cu $K\alpha_1 = 1.540563 \text{ \AA} \pm 5$ ppm, and Cu $K\alpha_2 = 1.544390 \text{ \AA} \pm 5$ ppm. Taking the *peak* wavelength values of $1537.400 \text{ xu} \pm 1$ ppm for the Cu $K\alpha_1$ and $1541.219 \text{ xu} \pm 6.5$ ppm for the Cu $K\alpha_2$ lines yields a wavelength conversion factor from angstrom to thousand x units of $\Lambda = 1.002057 \text{ \AA/kxu} \pm 5$ ppm. Recalculation of the best measurements in the literature with current values of the atomic weights gave values which agree with the present work within probable errors. Plane-ruled-grating measurements of x-ray wavelengths yield a value of $\Lambda = 1.00203 \pm 30$ ppm, which is lower than the above values, but the probable errors overlap.

INTRODUCTION

THE absolute (cm or \AA) scale of x-ray wavelengths has been established primarily by the ruled grating measurements¹⁻⁴ of a few x-ray lines which gave the correction factor⁵ 1.00203 for converting wavelengths in x units to m \AA . The impossibility of accurately

correcting Tyrén's concave grating measurements for the Lamb shift,⁶ DuMond and Kirkpatrick's⁷ difficulties in repeating Tyrén's measurements, theoretical questions,⁸ and the experimental problems involved in attempting to improve the plane grating measurements by the use of crystals for separating the α_1 , α_2 lines, emphasize the importance of establishing the x-ray wavelength scale by other methods. Actually only one set of plane grating measurements¹ is free of serious errors, and this has a probable error of 30 ppm.

Bragg⁹ was the first to calculate the grating constant

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¹ J. A. Bearden, *Phys. Rev.* **37**, 1210 (1931); **48**, 385 (1935).

² E. Bäcklin, *Z. Physik* **93**, 450 (1935).

³ M. Söderman, *Nature* **135**, 67 (1935).

⁴ F. Tyrén, *Z. Physik* **109**, 722 (1938); *Nova Acta Reg. Sci. (Uppsala)* **12**, No. 1 (1940).

⁵ R. T. Birge, *Am. J. Phys.* **13**, 63 (1945). In 1947 W. L. Bragg, M. Siegbahn, B. E. Warren, and H. Lipson recommended $\Lambda = 1.002020 \pm 0.000030$ for general adoption, *J. Sci. Instr.* **24**, 27 (1947); *Phys. Rev.* **72**, 437 (1947).

⁶ J. W. M. DuMond and E. R. Cohen, *Phys. Rev.* **103**, 1583 (1956).

⁷ J. W. M. DuMond and H. A. Kirkpatrick, Final Report to NSF, 1963 (unpublished).

⁸ J. A. Bearden and J. S. Thomsen, *Bull. Am. Phys. Soc.* **8**, 313 (1963); and W. C. Sauder, thesis, Department of Physics, Johns Hopkins University, 1963 (unpublished).

⁹ W. H. Bragg, *Proc. Roy. Soc. (London)* **88A**, 428 (1913); **89A**, 246 (1914); **89A**, 430 (1914).

of a crystal in cm from its molecular weight, density, and Avogadro's number. The Bragg equation, with correction for the refractive index of x rays in the crystal, may be written for a cubic crystal as

$$\lambda = \left(\frac{fA}{\rho N} \right)^{1/3} \frac{2 \sin \theta}{n(h^2 + k^2 + l^2)^{1/2}} \left[1 - \frac{\delta}{\sin^2 \theta} \right] \quad (1)$$

or

$$\lambda = \left(\frac{fA}{\rho N} \right)^{1/3} \frac{\lambda_{xu}}{a_{xu}}$$

λ is the wavelength in cm of an x-ray line diffracted by the crystal at an angle θ , A is the atomic (or molecular) weight of the crystal, ρ its density, N is Avogadro's number, h , k , and l are the Miller indices, n is the order of diffraction, f is the number of atoms in a unit cell ($f=8$ for silicon), δ is $1-\mu$, where μ is the index of refraction of the x ray in the crystal, and in the second alternative equation λ_{xu} is the wavelength in xu used to measure the grating constant a_{xu} . Recent experimental measurements have made possible a new least-squares adjustment of the atomic constants of higher precision than the 1955¹⁰ or 1957¹¹ values. The new value¹² of Avogadro's number with its probable error, is

$$N = 6.02252 \times 10^{23} (\text{g mole})^{-1} \pm 11 \text{ppm.}$$

Thus, the error in N contributes slightly more than 3 ppm to a wavelength measurement in Eqs. (1). The error in the atomic weight A , crystal imperfections, chemical impurities, etc., combined contribute an additional error which is the same order as that in N .

The variations in the grating constant¹³ of even the best optical quality calcite crystals emphasize the importance of making both the density and x-ray diffraction measurements on the same crystal sample. In fact, grating constant variations have been observed in optically clear calcite from one part of the crystal to another.¹³ Thus, it is important to make both measurements on small crystal samples consistent with good density measurements. In five researches¹⁴⁻¹⁸ only eleven different crystals have been reported in the literature where both density and x-ray diffraction measurements

were made on the same crystals, and seven of these were measured in the same laboratory.

In the past few years, procedures for chemically purifying and crystallizing silicon have produced large crystal samples of excellent quality, which suggests that these crystals may be a satisfactory replacement of calcite crystals for x-ray diffraction studies. Twenty-two carefully selected silicon crystals were obtained from four laboratories¹⁹ for the purpose of measuring the x-ray resolving power, unit cell dimensions, and density variations. The average dimensions of the crystals obtained were approximately $30 \times 40 \times 6$ mm, and with atomic planes (400), (111), (220), and (311) parallel to the large 30×40 -mm surface in various samples.

Two of these silicon crystals have been used, together with selected calcite and quartz crystals in a precision measurement of wavelengths (in all cases, the peak of the line²⁰) of the $K\alpha_1$ lines of tungsten, silver, molybdenum, and copper, and the $K\alpha_2$ line of chromium.²¹ A least-squares evaluation of the overdetermined ratios adjusted to the copper $K\alpha_1$ line as 1537.400 xu gave tungsten $K\alpha_1=208.58111$; silver $K\alpha_1=558.2595$; molybdenum $K\alpha_1=707.8448$; chromium $K\alpha_2=2288.899$, with a probable error of 1 ppm. Cohen and DuMond¹² have emphasized an apparent difference existing between previous crystal measurements of $N(\lambda/\lambda_{xu})^3$ observed when copper or molybdenum x rays were used. The consistency of the above values for 5 crystals and 5 wavelengths proves that this effect is in no way associated with the x-ray wavelengths or crystals used. Thus, the errors in the older density and x-ray measurements were probably larger than estimated.

APPARATUS AND MEASUREMENTS

X-Ray Equipment

The Société Genevoise double-crystal spectrometer was used for the measurement of the diffraction angles. The spectrometer circle was recalibrated with the aid of an angle-measuring interferometer²² and the usual four microscope observations. The error in the position of each of the 2160 circle division lines was measured by four observers, and the probable error calculated. The probable error in the position as read by the four microscopes was less than 0.1 sec for all the circle division lines.

¹⁹ We are greatly indebted to Dr. Walter Runyan of Texas Instruments, Inc., Dr. Maurice Tannenbaum of the Bell Telephone Laboratories, to the late Dr. W. C. Dash of the General Electric Company, and to Mr. Richard K. Wilcox of Knapp Electro-Physics, Inc., for their excellent cooperation in preparing the silicon crystals.

²⁰ J. A. Bearden, *Phys. Rev.* **43**, 94 (1933).

²¹ J. A. Bearden, A. Henins, J. G. Marzolf, W. C. Sauder, and J. S. Thomsen, *Phys. Rev.* **135**, A899 (1964), following paper. Usage of the copper $K\alpha_1=1537.400$ xu in previous works on the ratio of λ (angstroms) to λ (xu) suggests its continued use in the present report.

²² J. G. Marzolf, *Bull. Am. Phys. Soc.* **7**, 339 (1962); *Rev. Sci. Instr.* (to be published).

¹⁰ E. R. Cohen, J. W. M. DuMond, T. W. Layton, and J. S. Rollett, *Rev. Mod. Phys.* **27**, 363 (1955).

¹¹ J. A. Bearden and J. S. Thomsen, *Nuovo Cimento* **5**, 267 (1957); *Am. J. Phys.* **27**, 569 (1959).

¹² Committee on Fundamental Constants of the National Academy of Sciences, *Phys. Today* **17**, 48 (1964); also E. R. Cohen and J. W. M. DuMond, *Proceedings of the Second International Conference on Nuclidic Masses and Atomic Constants, Vienna, 1963* (Springer-Verlag, Berlin, to be published).

¹³ J. A. Bearden, *Bull. Am. Phys. Soc.* **7**, 339 (1962).

¹⁴ J. A. Bearden, *Phys. Rev.* **38**, 2089 (1931).

¹⁵ Y. Tu, *Phys. Rev.* **40**, 662 (1932).

¹⁶ M. Straumanis, A. Ievins, and K. Karlsons, *Z. Physik. Chem.* **B42**, 143 (1939).

¹⁷ G. Brogren, *Arkiv. Fysik* **7**, 47 (1953).

¹⁸ A. Smakula and J. Kalnajs, *Nuovo Cimento, Suppl. Ser. X*, **6**, 214 (1957); *Phys. Rev.* **99**, 1737 (1955); A. Smakula and V. Sils, *ibid.* **99**, 1744 (1955); A. Smakula, J. Kalnajs, and V. Sils, *ibid.* **99**, 1747 (1955).

The crystal on the main spectrometer axis was supported on a three-point support whose plane was made parallel to and on the axis of rotation.²¹ The parallelism was within one or two seconds, and the plane was off-axis by less than 0.01 mm. This precision of adjustment is important when measurements are made on imperfect crystal samples, where it is important that exactly the same area of the crystal be used for the diffraction in the two spectrometer positions. The first crystal was mounted on a three-point support midway between the main axis and the focal spot of the rotating target x-ray tube, and the plane formed by its three-point support was also adjusted parallel to the spectrometer axis to within less than 5 sec of arc. The surfaces of the crystals were ground and polished parallel to the atomic planes being used within 5 to 30 sec, which represents the crystal tilt alignment error. The center of the horizontal slit near the focal spot and the slit limiting the height of the x-ray beam entering the argon-filled proportional counter were adjusted in a plane perpendicular to the axis of the spectrometer within 60 sec.

The high voltage was obtained from a 3-phase 80 kV, 56-kW transformer equipped with full wave (silicon rectifiers) rectification. The voltage and current stabilization was the same as previously used in this laboratory.²³ A copper rotating target x-ray tube with a 0.6×10 mm focal spot was used as a source of x rays. The narrow x-ray beam was necessary to ensure diffraction measurements from the same small crystal area in the $(1 \pm n)$ measurements. The electronics for recording the proportional counter pulses were the usual nonoverloading amplifier, channel analyzer, and scaler-recorder.

X-Ray Wavelength and Corrections

Since the copper $K\alpha_{1,2}$ lines have been measured directly with the ruled gratings¹ and are also the most-used reference lines for crystallographic measurements, these lines have been used for the present diffraction angle measurements. Two lines have been used in order to minimize the probable errors due to fluctuations in measurements. The diffraction angle for these wavelengths is large, and the linewidths reasonably narrow, both of which increase the precision of the angular measurements.

The decrement from unity of the index of refraction, δ , which enters into Eq. (1), can be calculated from theory, or experimentally measured. In the present experiment it has been experimentally measured by the right-angle prism method²⁴ and found to be

$$\delta = (7.6 \pm 0.1) \times 10^{-6}$$

which corresponds to the calculated value of 7.5×10^{-6} . The experimental value has been used in computations.

²³ G. Schwarz and E. H. Byerly, *Rev. Sci. Instr.* **19**, 373 (1948).

²⁴ J. A. Bearden, *Phys. Rev.* **54**, 698 (1938).

The horizontal slit in front of the x-ray tube was 2.0 mm in height, and the one limiting the beam entering the proportional counter was 1.75 mm. The separation of the slits was 470 mm, and the angle correction calculated from the Williams²⁵ equation ranged from 0.07 to 0.35 sec. For all angles the relative correction to wavelength amounts to 1.3 ppm. The maximum tilt and misalignment errors of 30 and 60 sec noted in previous section give a correction of less than 0.01 sec (see following paper).

Density Measurement

The density was determined by hydrostatic weighing in water, using a Mettler M-5 microbalance with automatic weight-changing features and under-the-pan weighing attachment. In addition to the regular enclosure, the balance was further enclosed in a sheet aluminum housing to exclude air currents, and the experiment was performed in a room where the temperature was controlled to within $\pm 0.2^\circ\text{C}$ of 25°C . The weights were calibrated by weighing a set of National Bureau of Standards certified class *M* weights. The procedure for calculating the weight corrections from these weighings has been developed by Lashof and Macurdy.²⁶ These calculations also yield a probable error of weighing with the balance. On this particular balance the probable error of a single weighing was approximately 1 μg . During the weighings the air temperature inside the balance was monitored within $\pm 0.1^\circ\text{C}$, and the humidity inside the balance was measured with an electrical resistance-type hygrometer, with an error of less than 3%. The atmospheric pressure was measured to ± 0.2 mm of mercury in order to make the air buoyancy corrections.

The weighing chamber consisted of a triple-walled glass container as shown in Fig. 1, mounted beneath the balance. Water from a large constant temperature bath flowed at a rate of approximately 3 gallons/min around the inner chamber and returned via the outer jacket. The bath temperature was measured with two calibrated calorimeter-type (0.01°C per division) thermometers. The total probable error in the temperature determinations in the weighing chamber was estimated to be 0.004°C , which corresponds to approximately 1 ppm error in the water density.

A 0.001-in.-diam wire coated with platinum black to improve the surface wetting²⁷ was used to pass through the water surface. The crystals were supported on a small glass rod stirrup, (2), in Fig. 1, and the crystals could be lifted from this stirrup for the "empty" weigh-

²⁵ J. H. Williams, *Phys. Rev.* **40**, 636 (1932).

²⁶ T. W. Lashof and L. B. Macurdy, *Anal. Chem.* **26**, 707 (1954). The authors are indebted to L. B. Macurdy of the National Bureau of Standards for the loan of these class *M* weights and for a very informative discussion of precision weighing.

²⁷ P. Hidnert and E. L. Peffer, *NBS Circ. No. 487* (U. S. Government Printing Office, Washington, D. C., 1950); O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.* **64**, 758 (1942).

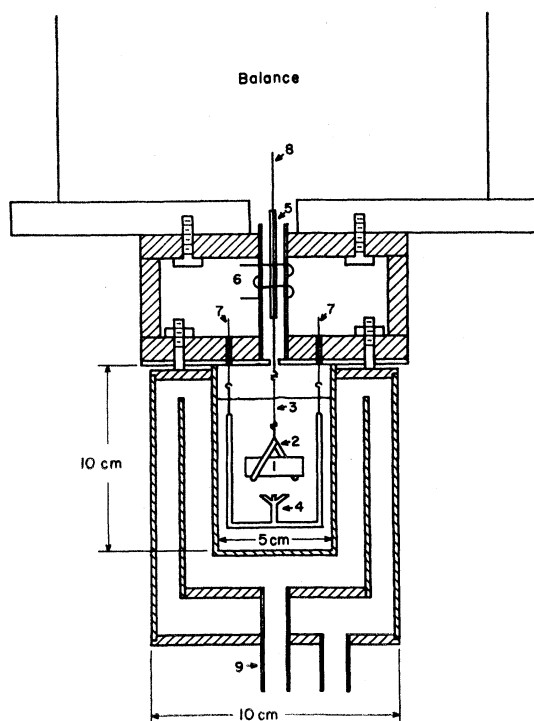


FIG. 1. Details of the weighing chamber. Legend: (1) crystal to be weighed, (2) crystal supporting stirrup, (3) 0.001-in.-diam platinum black-coated suspension wire, (4) lifter for raising crystal from stirrup, (5) nickel wire armature spot-welded to support wire, (6) 4-turn copper wire coil for magnetically deflecting the balance, (7) strings for raising crystal lifter, (8) support wire attached to balance pan hook, and (9) inlet for thermostating water.

ings by means of the lifting strings (7). Thus, it was possible to check the repeatability of the weighings by doing a series of weighings without removing the crystals from the weighing chamber. In addition to this, the balance could be deflected magnetically, thus producing motion of the suspension wire through the water surface, which made possible repeated determination of the balance point without arresting the balance. Repeatability indicated that the surface tension forces on the suspension were remaining constant.

The hydrostatic weighing method thus was refined until the remaining major source of error in the absolute density determination²⁸ is the uncertainty in the density of water. By definition the density of ordinary pure water at its maximum density (at approximately 4°C) is exactly 1 g/ml. Using the expansion coefficient of water then gives 0.9970751 g/ml at 25°C.²⁹ The accepted conversion factor³⁰ to cm^3 is $1.000028 \pm 0.000003 \text{ cm}^3/\text{ml}$,

which gives $0.997047 \pm 0.000003 \text{ g/cm}^3$ for the absolute density of water at 25°C. The water used in the experiment was triply distilled tap water, isotopic fractionating effects being avoided by discarding measured head and tail fractions of the distillate.³¹ The purity was checked by conductivity measurements³² which ranged from 1.1 to $1.7 \times 10^{-6} (\Omega \text{ cm})^{-1}$. The probable error introduced in the water density by the purification process is estimated not to exceed 1 ppm. The effects of dissolved air³³ and normal atmospheric pressure changes³⁴ on the density of water are negligible. However, in order to eliminate air bubble formation on the crystals being weighed, the water was boiled before using to expel the air.

The average probable error in determining the true mass of a 10-g crystal was approximately 0.2 ppm. This error includes the calibration of the balance weights, the precision of the balance, and the air buoyancy corrections. The average probable error for the weighings in water of the crystal of the same size was approximately 0.5 ppm. The major source of error in this is the variation of the surface tension effects on the thin suspension wire, therefore this error was computed from the variation of repeated weighings of the same crystal in water. The total experimental probable error of the individual density determinations was approximately 1.3 ppm.

Crystal Preparation

Seventeen of the 22 crystals were ground parallel to their respective atomic planes and polished. The remaining five were used for density measurements only. The accuracy of the parallelism between the surface and atomic planes ranged from 5 to 30 sec of arc. The crystals were etched in a 1:3:10 (by volume) solution of hydrofluoric, nitric, and glacial acetic acid for approximately 60 sec. The etching was barely perceptible by optical examination. Tests of the x-ray resolving power by measuring the (1-1) rocking curve indicated that no increase in the resolving power was observed after 20 sec of etching. Before the density measurements were made, the edges of the crystals were ground smooth and then further etched in a strong (1:3:3) etching solution to remove any possible loose particles from the surfaces.

The crystals were grown from high-purity intrinsic silicon and had very low dislocation densities as measured by the supplier. The oxygen concentration was measured by infrared absorption at 9- μ wavelength, and these are shown for each crystal in Table II.

²⁸ I. Henins, J. Res. Natl. Bur. Std. **68A**, No. 5 (1964).

²⁹ P. Chappuis, Travaux et Mémoires Bureau International des Poids et Mesures **13**, D1-D40 (1967); L. W. Tilton and J. K. Taylor, J. Res. Natl. Bur. Std. **18**, 205 (1937).

³⁰ J. W. M. DuMond, E. R. Cohen, and K. M. Crowe, *The Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957), p. 5.

³¹ N. Bauer and S. Z. Levin, in *Physical Methods of Organic Chemistry*, edited by A. Weissberger (Interscience Publishers, Inc., New York, 1959), Vol. 1, p. 136.

³² I. Kirshenbaum, *Physical Properties of Heavy Water* (McGraw-Hill Book Company, Inc., New York, 1951), pp. 269 and 295.

³³ W. Marek, Ann. Physik **44**, 171 (1891).

³⁴ N. E. Dorsey, *Properties of Ordinary Water Substances* (Reinhold Publishing Corporation, New York, 1940), p. 243.

ATOMIC WEIGHT OF SILICON

The atomic weight of silicon for this experiment was calculated by combining the best available data on isotopic abundances and nuclidic weights, as shown in Table I. Weighted averages for the abundances of Si²⁹

TABLE I. Isotopic abundances and weights of silicon.^a

| Si ²⁸ | Si ²⁹ | Si ³⁰ | Reference |
|--|--------------------------------|----------------------------------|-----------|
| Isotopic abundances (%) | | | |
| 92.28 ± 0.08 | 4.67 ± 0.05 | 3.05 ± 0.03 | b |
| 92.24 ± 0.10 | 4.69 ± 0.05 | 3.07 ± 0.05 | c |
| 92.27 ± 0.09 | 4.68 ± 0.05 | 3.05 ± 0.03 | d |
| 92.16 ± 0.06 | 4.71 ± 0.03 | 3.13 ± 0.04 | e |
| 92.19 ± 0.06 | 4.70 ± 0.03 | 3.12 ± 0.04 | f |
| 92.14 ± 0.20 | 4.73 ± 0.10 | 3.13 ± 0.10 | g |
| 92.18 ± 0.03 | 4.71 ± 0.02 | 3.12 ± 0.02 | h |
| Weighted averages | | | |
| 92.194 ± 0.020 | 4.702 ± 0.013 | 3.094 ± 0.013 | |
| Isotopic weights (C ¹² scale) | | | |
| 27.976927 ± 3 × 10 ⁻⁶ | 28.976491 ± 4.10 ⁻⁶ | 29.973761 ± 4 × 10 ⁻⁶ | i |

^a The isotopic abundance data are the same as those listed by G. H. Fuller, in *1959 Nuclear Data Tables*, edited by K. Way (U. S. Atomic Energy Commission, Washington, D. C., 1959), p. 66.

^b M. G. Ingram, *Phys. Rev.* **70**, 653 (1946).
^c E. P. Ney and J. H. McQueen, *Phys. Rev.* **69**, 41 (1946).
^d D. Williams and P. Yuster, *Phys. Rev.* **69**, 556 (1946).
^e J. R. White and A. E. Cameron, *Phys. Rev.* **74**, 991 (1948).
^f R. F. Hibbs, AECU-556, Dep., 1949 (unpublished).
^g J. F. Norton and P. D. Zemay, *J. Chem. Phys.* **20**, 525 (1952).
^h J. H. Reynolds, *Phys. Rev.* **90**, 1047 (1953).
ⁱ F. Everling, L. A. König, J. H. E. Mattauch, and A. H. Wapstra, *Nucl. Phys.* **15**, 342 (1960).

and Si³⁰ were formed, with weights proportional to the inverse squares of the probable errors quoted. The value for Si²⁸ was then obtained from the condition that the three abundances add up to 100%. (Other isotopes are reported only in insignificant amounts.) Fortunately, the same atomic weight is obtained by taking an unweighted mean of the tabulated values. Errors are quoted on the basis of internal, rather than external, consistency³⁵ since the former are more conservative. When these abundances are combined with the corresponding nuclidic weights, the result is

$$A = 28.0857 \pm 10 \text{ ppm},$$

which has been used in all wavelength calculations.

This value is consistent with that recently adopted by the IUPAC,³⁶ viz., 28.086 ± 0.001. This stated error is due chiefly to a small variation in the natural isotopic abundances of silicon, as reported by Allenby and reviewed by Rankama.³⁷ This should not be taken to indicate that the entire spread of values in Table I is primarily due to variations in natural abundances. The differences there appear consistent with the assigned errors and with those obtained for other elements in this region of the periodic table.

³⁵ R. T. Birge, *Phys. Rev.* **40**, 213 (1932).

³⁶ A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.* **84**, 4175 (1962).

³⁷ R. J. Allenby, *Geochim. Cosmochim. Acta* **5**, 40 (1954). K. Rankama, *Isotope Geology* (McGraw-Hill Book Company, Inc., New York 1954), p. 272.

RESULTS

The experimental results and the calculation of the x-ray wavelengths are summarized in Tables II and III. The first column lists the crystal identification by number. Column 2 records the individual crystal densities and the experimental probable error in ppm, and column 3 lists the measured oxygen content. The fourth column lists the crystal and atomic plane used as the first crystal on the double-crystal spectrometer. This crystal is essentially a collimator and principally influences only the width of the observed diffraction line. The measurements substantiate this fact. The fifth column indicates the order of diffraction by the first and second crystals of the spectrometer. The sixth column lists the atomic plane used in measuring the diffraction angle θ recorded in column 7, and column 8 the wavelengths calculated from Eq. (1), with $f=8$, $A = 28.0857$, $N = 6022.52 \times 10^{23}$ (g mole)⁻¹, and $\delta = 7.6 \times 10^{-6}$. Seventeen of the 22 crystals are listed, and the density of the remaining five crystals was measured, but the crystals were not of convenient size and shape for making the x-ray measurements. Table III is a similar table for the copper $K\alpha_2$ line. The averages of the wavelengths are

$$\lambda(\text{copper } K\alpha_1) = 1.540563 \text{ \AA} \pm 0.6 \text{ ppm},$$

$$\lambda(\text{copper } K\alpha_2) = 1.544390 \text{ \AA} \pm 0.5 \text{ ppm},$$

where the probable error quoted is due only to experimental errors in the x-ray measurement of the diffraction angles, the error in the measured densities, the actual variation in density and atomic weight due to the variation in the abundance ratios of the various samples, crystal dislocations, and other possible crystal defects that influence the diffraction angles or density.

In the Introduction the probable error in Avogadro's number was given as ±11 ppm. In the section on the atomic weight of silicon its probable error was given as ±10 ppm. The error in δ contributes less than 1 ppm to the errors in the wavelengths. The wavelengths in angstroms and their probable errors from Eq. (1) are

$$\lambda(\text{copper } K\alpha_1) = 1.540563 \text{ \AA} \pm 5 \text{ ppm},$$

$$\lambda(\text{copper } K\alpha_2) = 1.544390 \text{ \AA} \pm 5 \text{ ppm}.$$

The silicon crystals were from four different laboratories, and the excellent agreement of the wavelengths for the different crystals indicates a constant abundance ratio of the isotopes composing the crystals used. It is possible that the silicon used in growing the crystals came from a single source, but most probably they had a different origin. Abundance ratios of the crystals used should be measured, and this will be attempted. From the results in Tables II and III it is evident that the x-ray and density measurements can be used as a means of determining small variations in the atomic weight of silicon.

If we provisionally define the x-unit scale by taking

TABLE II. The wavelength in Å of the copper $K\alpha_1$ line by Eq. (1).

| Silicon crystal | Density \pm ppm g/cm ³ | (O atoms/ cm ³) $\times 10^{-17}$ | First crystal | Order of diffraction | Crystal plane | Diffraction angle θ | Wavelength Eq. (1) Å |
|-----------------|--|--|--------------------|----------------------|---------------|----------------------------|----------------------|
| 2 | 2.329011 \pm 1.2 | 7.3 | Si(111) | (1 \pm 1) | (111) | 14° 13' 21.5" | 1.540555 |
| 2 | 2.329011 \pm 1.2 | 7.3 | Si(111) | (1 \pm 1) | (111) | 14° 13' 21.8" | 1.540564 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 13' 21.4" | 1.540554 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 13' 21.6" | 1.540560 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 13' 22.6" | 1.540589 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 13' 22.3" | 1.540581 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 13' 21.4" | 1.540554 |
| 1 | 2.329009 \pm 1.1 | 7.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.5" | 1.540560 |
| 2 | 2.329011 \pm 1.2 | 7.3 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 33.5" | 1.540567 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.5" | 1.540562 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.9" | 1.540565 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (3 \pm 3) | (111) | 47° 28' 31.3" | 1.540554 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (3 \pm 3) | (111) | 47° 28' 31.7" | 1.540557 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.1" | 1.540559 |
| 4 | 2.328995 \pm 1.2 | 8.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.4" | 1.540563 |
| 5 | 2.329010 \pm 1.6 | 6.2 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 31.6" | 1.540554 |
| | 2.329010 \pm 1.6 | | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | | 47° 28' 31.8" | 1.540556 |
| 6 | 2.329008 \pm 1.5 | 6.6 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 28' 32.9" | 1.540563 |
| 9 | 2.329000 \pm 1.7 | 7.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.2" | 1.540563 |
| 10 | 2.328986 \pm 1.4 | 7.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 6.5" | 1.540555 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.2" | 1.540560 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Si(220) | (1 \pm 1) | (220) | 23° 39' 6.8" | 1.540553 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Si(220) | (1 \pm 1) | (220) | 23° 39' 7.8" | 1.540570 |
| 12 | 2.329021 \pm 1.2 | 7.6 | Si(220) | (1 \pm 1) | (220) | 23° 39' 7.6" | 1.540565 |
| 12 | 2.329021 \pm 1.2 | 7.6 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.5" | 1.540564 |
| 13 | 2.329006 \pm 1.4 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.0" | 1.540558 |
| 13 | 2.329006 \pm 1.4 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.6" | 1.540569 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.5" | 1.540567 |
| | 2.329004 \pm 1.5 | | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 6.8" | 1.540556 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Si(220) | (1 \pm 1) | (220) | 23° 39' 6.1" | 1.540544 |
| 15 | 2.328998 \pm 1.4 | 3.4 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 39' 7.4" | 1.540567 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 42.3" | 1.540573 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Si(311) | (1 \pm 1) | (311) | 28° 3' 42.2" | 1.540572 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Si(311) | (1 \pm 1) | (311) | 28° 3' 41.1" | 1.540557 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Si(311) | (1 \pm 1) | (311) | 28° 3' 41.2" | 1.540558 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 41.3" | 1.540559 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 42.2" | 1.540571 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 42.2" | 1.540571 |
| 18 | 2.329008 \pm 1.2 | | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 40.5" | 1.540540 |
| 18 | 2.329008 \pm 1.2 | | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 3' 41.2" | 1.540556 |
| 12 | 2.329021 \pm 1.2 | 7.6 | Qz(10 $\bar{1}$ 1) | (1 \pm 2) | (220) | 53° 21' 12.7" | 1.540559 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 2) | (220) | 53° 21' 14.4" | 1.540553 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 2) | (220) | 53° 21' 13.3" | 1.540567 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 2) | (220) | 53° 21' 12.2" | 1.540560 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 2) | (220) | 53° 21' 12.2" | 1.540560 |
| 8 | 2.329000 \pm 1.0 | 1.3 | Single crystal | | (400) | 34° 33' 55.7" | 1.540560 |

the value^{20,38} 1537.400 xu for the wavelength of the peak of Cu $K\alpha_1$, Table II now gives the conversion factor

$$\Lambda = 1.002057 \pm 5 \text{ ppm.}$$

The probable error is almost entirely due to uncertainties in the atomic weight of silicon A , and in Avogadro's number N . No error has been included for the wavelength of Cu $K\alpha_1$ in xu, since this is treated here as a defined value.

In the above paper³⁸ the Cu $K\alpha_2$ wavelength was 1541.219 xu; and the probable error in this figure (relative to Cu $K\alpha_1$) is about 6.5 ppm. Hence it follows from Table III that

$$\Lambda = 1.002057 \pm 8 \text{ ppm.}$$

Statistically this does not improve our knowledge of the

conversion factor Λ , but experimentally it indicates that no important error has arisen due to the use of a line of lower intensity, greater width, and higher asymmetry. Furthermore the Cu $K\alpha_2$ data provide a precision measurement of the α_1 , α_2 separation, probably the most accurate ever made on this doublet.

COMPARISON OF RESULTS WITH PREVIOUS MEASUREMENTS

Smakula¹⁸ and his collaborators have measured the density and x-ray diffraction angles for seven different kinds of crystals. The density measurements were made with a technique very similar to that employed in the present work. The x-ray measurements, however, were made with a powder diffraction technique, where the shape and angular position of the diffraction lines are determined by instrument alignment, primary beam

³⁸ J. A. Bearden and C. H. Shaw, Phys. Rev. 48, 18 (1935).

TABLE III. The wavelength in Å of the copper $K\alpha_2$ line by Eq. (1).

| Silicon crystal | Density \pm ppm g/cm ³ | (O atoms/ cm ³) $\times 10^{-17}$ | First crystal | Order of diffraction | Crystal plane | Diffraction angle θ | Wavelength Eq. (1) Å |
|-----------------|--|--|--------------------|----------------------|---------------|----------------------------|----------------------|
| 1 | 2.329009 \pm 1.1 | 7.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.8" | 1.544386 |
| 1 | 2.329009 \pm 1.1 | 7.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.9" | 1.544387 |
| 2 | 2.329011 \pm 1.2 | 7.3 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.8" | 1.544385 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.3" | 1.544384 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.2" | 1.544384 |
| 4 | 2.328995 \pm 1.2 | 8.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.9" | 1.544390 |
| 5 | 2.329010 \pm 1.6 | 6.2 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 51.1" | 1.544381 |
| 5 | 2.329010 \pm 1.6 | 6.2 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 52.1" | 1.544388 |
| 6 | 2.329008 \pm 1.5 | 6.6 | Qz(10 $\bar{1}$ 1) | (1 \pm 3) | (111) | 47° 37' 52.0" | 1.544387 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 15' 31.6" | 1.544392 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 15' 31.2" | 1.544380 |
| 3 | 2.329001 \pm 1.1 | 8.7 | Si(111) | (1 \pm 1) | (111) | 14° 15' 31.6" | 1.544392 |
| 9 | 2.329000 \pm 1.7 | 7.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 52.0" | 1.544396 |
| 10 | 2.328986 \pm 1.4 | 7.7 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 51.2" | 1.544386 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 51.6" | 1.544386 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Si(220) | (1 \pm 1) | (220) | 23° 42' 51.1" | 1.544388 |
| 11 | 2.329013 \pm 1.2 | 7.3 | Si(220) | (1 \pm 1) | (220) | 23° 42' 51.8" | 1.544390 |
| 12 | 2.329021 \pm 1.2 | 7.6 | Si(220) | (1 \pm 1) | (220) | 23° 42' 51.1" | 1.544376 |
| 12 | 2.329021 \pm 1.2 | 7.6 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 52.1" | 1.544393 |
| 13 | 2.329006 \pm 1.4 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 51.2" | 1.544381 |
| 13 | 2.329006 \pm 1.4 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 52.3" | 1.544400 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 52.1" | 1.544397 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 52.2" | 1.544399 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Si(220) | (1 \pm 1) | (220) | 23° 42' 51.8" | 1.544392 |
| 14 | 2.329004 \pm 1.5 | 3.5 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 51.2" | 1.544382 |
| 15 | 2.328998 \pm 1.4 | 3.4 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (220) | 23° 42' 51.8" | 1.544393 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Si(311) | (1 \pm 1) | (311) | 28° 8' 14.8" | 1.544390 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Si(311) | (1 \pm 1) | (311) | 28° 8' 14.2" | 1.544382 |
| 16 | 2.329001 \pm 1.3 | 2.4 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 15.1" | 1.544394 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 14.2" | 1.544381 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 15.8" | 1.544403 |
| 17 | 2.329004 \pm 1.1 | 3.8 | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 14.8" | 1.544389 |
| 18 | 2.329008 \pm 1.2 | | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 14.2" | 1.544380 |
| 18 | 2.329008 \pm 1.2 | | Qz(10 $\bar{1}$ 1) | (1 \pm 1) | (311) | 28° 8' 14.8" | 1.544388 |

width and intensity distribution, detector slit, sample flatness and displacement from axis, penetration of x rays, and vertical divergence of the x-ray beam. These factors were considered and corrections estimated or calculated. Pike³⁹ has calculated for the diffractometer used by Smakula *et al.* a 40 ppm increase in lattice constant due to vertical divergence for center of gravity diffraction measurements. However, Smakula⁴⁰ used the peak of the diffraction line, and his recalculations of his data with the center of gravity method and Pike's correction equation gave values in accord with the 1955 published values.

In column 2 of Table IV we have recorded the measured lattice spacings in x units obtained by dividing the published values by the ratio of 1.54051 Å/1.537400 kxu. Smakula⁴⁰ estimates that the probable error does not exceed 20 ppm. The measured densities and errors are listed in column 3, and the atomic and molecular weights with an estimated probable error in column 4. The lattice spacings in Å as calculated from Eq. (1) are shown in column 5, and in column 6 the ratio Λ of these to the measured lattice spacings in x units. The estimated probable errors include ± 20 ppm for the x-ray measurements plus those of the densities and molecular

weights as shown. The error assigned to the average has been estimated on the assumption that the 20-ppm error in measurement of grating constants is largely a systematic one common to all crystals. Likewise a common error exists in the density determinations due to a 3-ppm uncertainty in the density of water and the error in the measured ratio of the density of water to that of the quartz standard employed.

The values of Λ are in good agreement, and the use of seven different crystals is of great importance in minimizing the effects of the atomic weight errors in determining the conversion factor Λ by the Bragg method.

TABLE IV. Wavelengths calculated from the data of Smakula *et al.*^a based on copper $K\alpha_1 = 1537.400$ xu and the 1961 values^b of the atomic weights on C¹² scale.

| Crystal | Lattice spacing xu | Density 25°C \pm ppm | Atomic or Mol wt \pm ppm | Lattice spacing Å | $\Lambda \pm$ ppm |
|------------------|--------------------|------------------------|----------------------------|-------------------|-------------------|
| Al | 4041.42 | 2.69801 \pm 10 | 26.9815 \pm 5 | 4.04982 | 1.002078 \pm 23 |
| CaF ₂ | 5452.39 | 3.17934 \pm 16 | 78.077 \pm 13 | 5.46365 | 1.002065 \pm 25 |
| CsI | 4558.50 | 4.52593 \pm 27 | 259.808 \pm 5 | 4.56798 | 1.002080 \pm 33 |
| Ge | 5646.12 | 5.32674 \pm 10 | 72.628 \pm 14 | 5.65786 | 1.002079 \pm 25 |
| TlCl | 3834.71 | 7.01829 \pm 10 | 239.82 \pm 35 | 3.84260 | 1.002057 \pm 40 |
| TlBr | 3977.83 | 7.45292 \pm 10 | 284.28 \pm 35 | 3.98610 | 1.002079 \pm 40 |
| Si | 5419.76 | 2.32904 \pm 9 | 28.0857 \pm 10 | 5.43093 | 1.002061 \pm 20 |
| | | | | Average | 1.00207 \pm 20 |

³⁹ Pike, J. Sci. Instr. 34, 355 (1957).⁴⁰ A. Smakula (private communication).^a See Ref. 18.^b See Ref. 36.

TABLE V. Measurements with Mo $K\alpha_1 = 707.845$ xu (Cu $K\alpha_1 = 1537.400$ xu).

| Crystal | Lattice spacing xu | Temp. (°C) | Density | Atomic weight ^e | Wavelength Å | Λ |
|------------------------|---------------------------------|------------|----------------------|----------------------------|--------------|-------------------------|
| Calcite ^a | 3029.55 | 20 | 2.71026 | 100.094 | 0.709289 | 1.00204 |
| Calcite ^b | $a = 4980.12$ $c = 17025.45$ | 20 | 2.71029 ^a | 100.094 | 0.709298 | 1.00204 |
| Calcite ^c | 3029.49 | 18 | 2.71003 | 100.094 | 0.709312 | 1.00207 |
| Diamond A ^e | 3559.77 | 18 | 3.51543 ^d | 12.0111 | 0.709290 | 1.00204 |
| Diamond B ^e | 3559.67 | 18 | 3.51543 ^d | 12.0111 | 0.709309 | 1.00207 |
| Quartz ^b | $a = 4902.98$ $c = 5393.73$ | 18 | 2.64908 | 60.0845 | 0.709297 | 1.00205 |
| Average | | | | | | 1.00205 ± 20 ppm |

^a See Ref. 14.^b See Ref. 17.^c See Ref. 15.^d See Ref. 24.^e See Table IV. The calcite values have been increased 40 ppm because of chemical impurities. See J. A. Bearden and J. S. Thomsen, *Nuovo Cimento* 5, 1 (1957). ϕ calcite = 1.09598 at 20°, A. Henins, *Bull. Am. Phys. Soc.* 9, 387 (1964).

The average value of the conversion factor from the Smakula *et al.* data in Table IV is

$$\Lambda = 1.00207 \pm 20 \text{ ppm.}$$

X-ray and density measurements have also been made on calcite,^{14,15,17} diamond,¹⁵ and quartz crystals¹⁷ with the Mo $K\alpha_1$ radiation.²⁰ The x-ray measurements were made on single crystals with either a double-crystal or tube spectrometer, and do not involve the extensive corrections of the powder diffraction technique. However, there are only two measurements^{14,15} in which both the density and x-ray diffraction measurements were made on the same crystal sample. The measured lattice spacings in x units, the densities, atomic and molecular weights used, calculated lattice spacing in Å, and the conversion factor for each crystal are shown in Table V.

Brogren¹⁷ did not measure the density of either the calcite or quartz crystals. For calcite he used the average value of $\rho = 2.71029$, and for quartz he calculated the density from Batuecas⁴¹ measurements, which were made at 0° and corrected to 18° by the expansion coefficients. The latter value is in good agreement with the measurements made by Smakula *et al.*¹⁸ Tu¹⁵ reported considerable difficulty in measuring the density of diamond, and obtained a very low value, which if used gives a conversion factor of $\Lambda = 1.00218$, indicating a serious error in his density measurements. Hence we have used his x-ray data on the two diamonds, A and B, and the density measured by Bearden²⁴ to obtain the values in Table V. Tu's value for the density of calcite is also extremely low, and the Λ calculated from his calcite measurements therefore is high. Tu¹⁵ also attempted to measure the density and x-ray diffraction angles for rock salt and potassium chloride, but because of the poor quality of such crystals his measurements are too inaccurate to warrant inclusion in Table V.

It is difficult to estimate a probable error for these results, since most of the density and x-ray measure-

ments were made on different crystal samples, and in two instances we have revised the author's measured density. We have taken ± 20 ppm as an estimated error of the mean, and obtain from Table V

$$\Lambda = 1.00205 \pm 20 \text{ ppm.}$$

DuMond and Cohen¹² have calculated NA^3 (to eliminate correlations in input data for atomic constants calculations) for the measurements recorded in Tables IV and V, and with a statistical analysis emphasize the difference in the average value of NA^3 computed in the two tables. However, with the estimated probable errors given here the two sets of data appear quite consistent.

The value of the conversion factor Λ can be directly obtained from the ruled grating measurements; results of Bearden,¹ Backlin,² and Tyrén⁴ are shown in Table VI. However, Sandström⁴² has pointed out that the wavelength of the aluminum $K\alpha_{1,2}$ line is strongly dependent on the chemical state of the emitter, and

TABLE VI. Ruled grating measurements.

| Date | Line | Grating wavelength (Å) | Crystal wavelength (kxu) | Λ |
|-------------------|--------------------|------------------------|--------------------------|-----------|
| 1931 ^a | Cu $K\beta_{1,3}$ | 1.39225 | 1.389364 ^b | 1.00208 |
| 1931 ^a | Cu $K\alpha_{1,2}$ | 1.54172 | 1.538675 ^b | 1.00198 |
| 1931 ^a | Cr $K\beta_{1,3}$ | 2.08478 | 2.080590 ^b | 1.00201 |
| 1931 ^a | Cr $K\alpha_{1,2}$ | 2.29097 | 2.286310 ^b | 1.00204 |
| 1935 ^e | Al $K\alpha_{1,2}$ | 8.3395 | 8.32290 ^d | 1.00199 |
| 1935 ^e | Cu $K\alpha_1$ | 1.5406 | 1.53740 ^b | 1.00208 |
| 1940 ^f | Various | | | 1.00199 |

^a See Ref. 1.^b See Ref. 38.^c See Ref. 2.^d A. Larsson, dissertation, Uppsala University Arsskr. 1929 (unpublished).^e See Ref. 46.^f See Ref. 4.⁴¹ T. Batuecas, *Nature* 159, 705 (1947).⁴² A. E. Sandström, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 240.

Bjorkman⁴³ working with aluminum K x rays found that reproducibility was impossible with current techniques. Cohen and DuMond⁶ have pointed out that Tyrén's⁴ excellent concave grating measurements can not be accurately corrected for the Lamb shift, but an approximate correction would raise his published value of 1.00199 to approximately 1.00203. Recent theoretical⁴⁴ and experimental work has shown that the copper $K\alpha_1$ line measured with a large grating⁴⁵ and double-crystal spectrometer technique is also open to serious question. Deleting Backlin's and Tyrén's aluminum values and the double-crystal spectrometer result for the above reasons leaves only the first four plane ruled grating values in Table VI. The "limiting" error in these copper and chromium measurements was estimated as 100 ppm and this is usually regarded as approximately 3σ . Thus the ruled grating result becomes

$$\Lambda = 1.00203 \pm 30 \text{ ppm.}$$

The value of the conversion constant Λ has recently⁴⁶ been obtained from a very precise measurement of the high-frequency limit of the continuous x-ray spectrum measured with a mercury vapor target x-ray tube. The isochromats of the high-frequency limit were very sharp and exhibited no fine structure, which had previously limited the precision of evaluating the cutoff point. Combining this result with the recommended value¹² of h/e gives

$$\Lambda = 1.002005 \pm 24 \text{ ppm.}$$

The total voltage corrections (for work function, space charge, etc.) to the 8-kV x-ray voltage were less than 1.0 V; it would require a 0.4 V decrease in this quantity to raise the resulting value of Λ into agreement with the others. The correction for space charge⁴⁷ is less than 0.1 V, unless the conditions under which this term was originally calculated and experimentally verified differ drastically from those existing in the x-ray tube. The average values of the conversion constant Λ from the tables and from the high-frequency limit of the continuous x-ray spectrum are shown in Table VII. The

TABLE VII. Values of the conversion constant Λ .

| | |
|----------------------|----------------------|
| Table II | 1.002057 \pm 5 ppm |
| Table III | 1.002057 \pm 7 ppm |
| Table IV | 1.00207 \pm 20 ppm |
| Table V | 1.00205 \pm 20 ppm |
| Table VI | 1.00203 \pm 30 ppm |
| High-frequency limit | 1.00201 \pm 25 ppm |

agreement is in general satisfactory except for the high-frequency limit value.

CONCLUSIONS

The absolute scale of x-ray wavelengths has been evaluated by precision measurements of the density and x-ray diffraction angles on seventeen selected silicon crystals from four sources. The uniformity of the density and x-ray measurements indicated that dislocations, residual impurities, and crystal imperfections do not seriously affect the physical characteristics of the crystal.

The value of the conversion constant Λ from the silicon measurements appears to be more precise than any previous measurement by any method, and it is consistent with the previous results within the estimated probable errors.

New experimental measurements are in progress which will furnish additional data on the conversion constant Λ and a weighted average will be recommended when these are reported.

Note added in proof. A private communication from Professor Bengt Edlén reports that he and L. A. Svensson have remeasured the Al $K\alpha$ lines on Tyrén's original plates and obtained a new value of Λ in apparent agreement with the present result. A paper describing this work has been accepted by Arkiv. Fysik.

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⁴³ L. E. Bjorkman, thesis, Uppsala, 1954 (unpublished).

⁴⁴ W. C. Sauder, thesis, Department of Physics, The Johns Hopkins University, 1963 (unpublished).

⁴⁵ J. A. Bearden, Phys. Rev. **48**, 385 (1935).

⁴⁶ Jon J. Spijkerman and J. A. Bearden, Phys. Rev. **134**, A871 (1964).

⁴⁷ E. G. Linder and K. G. Hernqvist, J. Appl. Phys. **21**, 1088 (1950).