

X-Ray Wavelength Conversion Factor $\Lambda(\lambda_g/\lambda_s)^*$

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A new experimental value of the x-ray conversion factor Λ ($\text{m}\text{\AA}/\text{xu}$) has been obtained through a precision experiment on calcite crystals, and a recommended value of Λ adopted based on this and other data. Nine selected crystals were used and the principal impurities determined by spectrochemical analysis. Grating constants were measured with the $\text{Cu } K\alpha_1$ and $\text{Ag } K\alpha_1$ emission lines, and the density of each crystal obtained by hydrostatic weighing in ethylene bromide. The product ρd^3 for an ideal impurity-free crystal was then computed by a linear extrapolation, with a least-squares adjustment to determine coefficients. The geometrical volume factor Φ was found by experimental measurement of dihedral angles on five of the crystals. Combining these data with the best available values for atomic weight and Avogadro's number yields $N\Lambda^3 = (6.05972 \pm 0.00015) \times 10^{23} (\text{g mole})^{-1} (\text{m}\text{\AA}/\text{xu})^3$ and $\Lambda = 1.002055 \text{ m}\text{\AA}/\text{xu}$, where the x unit is based on $\lambda_{\text{Cu } K\alpha_1} = 1537.400 \text{ xu}$. Taking a weighted average of this result and other high-precision data on Λ has led to the adoption of $\Lambda = (1.002056 \pm 0.000005) \text{ m}\text{\AA}/\text{xu}$ expressed on the same basis. The result becomes $\Lambda = (1.002076 \pm 0.000005) \text{ m}\text{\AA}/\text{xu}$ when referred to an x-unit scale on which $\lambda_{\text{W } K\alpha_1} = 208.5770 \text{ xu}$. This last wavelength then becomes $\lambda_{\text{W } K\alpha_1} = 0.2090100 \text{ \AA}$, which value has been adopted by the author as a wavelength standard.

I. INTRODUCTION

IN 1913, Bragg¹ calculated the grating constant of a crystal in terms of its molecular weight, density, and Avogadro's number. For a rhombohedral crystal, the relationship between these quantities is given by

$$N = fM/\rho d^3\Phi, \quad (1)$$

where N is Avogadro's number, f is the number of atoms per unit cell, M the molecular weight, ρ the density, d the grating constant, and Φ a geometrical factor giving the volume of the rhombohedral cell of unit height. If Λ denotes the conversion factor between x units and milliangstroms ($\text{m}\text{\AA}/\text{xu}$), this equation may be rewritten as

$$\Lambda^3 = fM/\rho d'^3\Phi N, \quad (2)$$

where d' is the grating constant measured in terms of xu. The quantity d' is obtained through measurement of the Bragg angle for a line whose wavelength is known in terms of xu.

This relation has been used many times to determine Avogadro's number through measurements on crystals. It may also be used as a means of measuring Λ experimentally. Since all the quantities except d' will then appear to the $\frac{1}{3}$ power, the result becomes rather insensitive to errors in such variables. Henins and Bearden² have recently reported such a measurement in this laboratory, using silicon crystals (since silicon has a cubic crystal structure, Φ is equal to unity in this instance).

Calcite is probably the most commonly used crystal in x-ray spectroscopy and may also be employed in Eq. (2) for the determination of Λ . A vast amount of data³ is available on Bragg angles of various x-ray lines with calcite (its grating constant has, in fact, been used

as a definition of the x unit); there have been a number of excellent density determinations for such crystals. However, for high-precision work it is necessary to measure grating constant and density of the same crystal sample; in most cases this has not been done. Furthermore, the problem is complicated by the presence of appreciable amounts of impurities in even the best calcite samples. In many cases, such impurities are of the order of 100 ppm (parts per million) and thus can produce a significant error in the computed value of Λ .

As is well known and is shown again in the present work, most of the impurities in a calcite crystal are in the form of positive ions. There are two ways in which they might occur in the crystal: substitutional impurities, i.e., impurity ions replacing the calcium ions in a few of the unit cells; or interstitial impurities, i.e., impurity atoms occurring in a few unit cells in addition to those atoms normally found in the calcite crystal structure. Consider the effect of a single impurity. If the ratio of impurity ions to calcium ions is denoted by X , the effective molecular weight of the crystal will be given by

$$M_{\text{eff}} = M[1 + (X\Delta M/M)], \quad (3)$$

where M is the molecular weight of an ideal crystal and ΔM is the change in molecular weight for a unit cell containing the impurity. If the impurity is substitutional and replaces calcium, this will be given by

$$\Delta M_{\text{sub}} = M_i - M_{\text{ca}}, \quad (4)$$

where M_i and M_{ca} are the atomic weights of the impurity and of calcium, respectively. This correction can be either positive or negative. On the other hand, if the impurity is interstitial, the change will be simply

$$\Delta M_{\text{int}} = M_i, \quad (5)$$

which is always positive. Obviously, the effect will be considerably greater for an interstitial impurity, par-

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¹ W. L. Bragg, Proc. Roy. Soc. (London) **A88**, 428 (1913).

² I. Henins and J. A. Bearden, Phys. Rev. **135**, A890 (1964).

TABLE I. Crystals, origins (if known), and impurity contents. Impurities of less than 5 ppm have been omitted in this tabulation.

Crystal	Origin	Impurities (ppm)		
		Magnesium	Manganese	Strontium
1	Mexico	40	300	40
2	unknown	60	150	20
3	unknown	0	70	50
4	unknown	0	40	10
5	South America	30	50	160
6	unknown	0	20	15
7	Iceland	0	60	200
8	unknown	0	80	150
9	unknown	0	60	150

ticularly if the atomic weight of the impurity is quite close to that of calcium.

Birge³ analyzed impurity data on crystals used in previous Bearden⁴ experiments and obtained, assuming substitutional impurities, a correction of 31 ppm to be added to the molecular weight of calcite. Brogren⁵ later used an average based on impurity data of both Bearden and Straumanis and Dravmijs,⁶ obtaining an average correction of 50 ppm. Both corrections are based on the assumption of substitutional impurities; neither can give more than an order-of-magnitude estimate when applied to other calcite crystals.

The present investigation was designed to attain a high-precision value of $N\Lambda^3$, and hence of Λ , with calcite crystals. Nine different samples have been studied; measurements of both density and grating constant have been carried out on each sample. In addition, each crystal has been analyzed for chemical impurities. The resulting data have been used in an attempt to obtain the properties of an ideal impurity-free calcite crystal by extrapolation.

II. MEASUREMENTS AND DATA

A. Crystals

Nine samples of calcite crystals were selected for this work. They were obtained from a wide variety of different sources and suppliers. The geographical sources of the crystals, where known, are listed in Table I. Most of the crystals were of high quality for x-ray work; however, one of high chemical impurities (No. 1, the Mexican crystal) was deliberately included.

B. Chemical Analysis

These crystals were all analyzed for impurities by spectrochemical analysis.⁷ All crystals except No. 2 and No. 8 were analyzed for the presence of more than 20 possible impurities, nearly all metallic. In most cases,

³ R. T. Birge, *Am. J. Phys.* **13**, 63 (1945).

⁴ J. A. Bearden, *Phys. Rev.* **38**, 2089 (1931).

⁵ G. Brogren, *Arkiv Fysik* **7**, 47 (1953).

⁶ M. Straumanis and A. Dravmijs, *Z. Anal. Chem.* **120**, 168 (1940).

⁷ Analysis performed by Ledoux & Company, Teaneck, New Jersey.

the impurity content was too low to be detectable (less than 5 ppm and in some cases less than 2 ppm). For several other elements it was just detectable, but still under 10 ppm. Three impurities were present in significant amounts (order of 100 ppm); magnesium, manganese, and strontium. Crystals 2 and 8 were analyzed at a later date for these three impurities only. The data on these impurities are given in Table I; impurity contents listed there represent *weight ratio* of impurity to total weight of crystal. These values are estimated to be correct to $\pm 25\%$ of the amount reported.

C. Density Determinations

The densities of the various samples were determined to high precision by hydrostatic weighing, using the basic procedure reported by Henins.⁸ However, since the calcite crystals were slightly soluble in water, it was decided to use ethylene bromide ($C_2H_4Br_2$) as the liquid for immersion.

The density of the ethylene bromide was determined relative to water by using a silicon crystal as a transfer standard. With the density of water taken as (0.997047 ± 0.000003) g/cm³ at 25°C, three calibration runs gave density values of 2.167060, 2.167119, and 2.167121 g/cm³. The first value, about 27 ppm lower than the average of the last two, was used with Crystal No. 4, the density of which was measured immediately after the first calibration. A lapse of about ten days occurred without further measurements; then the density determinations for the eight remaining calcite crystals, as well as the last two calibration runs, were made within a four-day period. The average density of the liquid given by the last two calibration measurements was used for these eight cases. While the reason for variation in density of the ethylene bromide is still unexplained, consistency of the resulting data indicates that the effect is probably real.

All of the crystal densities involve a systematic probable error of about 3 ppm, due to the uncertainty in the density of water. In addition, there is a random error of 2 ppm in the various individual determinations, which fixes the accuracy of *relative* density values. The first crystal measured, No. 4, should perhaps be assigned a higher error due to the variation in the density of the ethylene bromide, as discussed above. However, this one case was not considered sufficiently important to warrant the complication of unequal weights. The consistency of the results seems to justify the procedure adopted.

D. Grating Constants

Grating constants of the various calcite crystals were measured with a double-crystal spectrometer using the $Cu K\alpha_1$ and $Ag K\alpha_1$ lines. The instrument employed and the method of measuring Bragg angles have been

⁸ I. Henins, *J. Res. Natl. Bur. Std.*, (to be published).

described by Bearden *et al.*⁹ Small corrections for temperature, index of refraction, and vertical divergence were made, as described in this reference.

The Cu $K\alpha_1$ and Ag $K\alpha_1$ series of measurements were separated by more than a year; various adjustments to the spectrometer and slit system had been made in the interim, so that any common systematic errors should have been minimal.

The results are shown in Table II. These values are based on an assumed wavelength of 1537.400 xu for Cu $K\alpha_1$, together with the wavelength ratio of Cu $K\alpha_1$ to Ag $K\alpha_1$ obtained by Bearden *et al.*,⁹ which gives 558.2594 xu for the latter. The two series of measurements are in agreement within statistical errors. In the calculations to follow, an average of the two values has been adopted. All wavelengths refer to *peak* values.

In the study cited above,⁹ it was indicated that an average systematic error of 3.6 ppm occurred between different series of runs, presumably due to small alignment errors. The alignment procedure has now been further refined and the two series of runs reported here show no indication of any systematic difference. Nevertheless, a 2-ppm systematic error in d' will be included in the final computation of probable error.

E. Determination of Φ

The geometrical factor Φ is obtained through measurement of the obtuse dihedral angle α ($\alpha \approx 105^\circ$) between two crystal faces.

$$\Phi = (1 + \cos\beta)^2 / (1 + 2 \cos\beta) \sin\beta \quad (6)$$

where $\cos\beta = (\cos\alpha) / (1 - \cos\alpha)$ or, more simply,

$$1/\Phi = (1 + \cos\alpha)(1 - 2 \cos\alpha)^{1/2}. \quad (7)$$

The angle α was experimentally measured on 5 of the 9 crystals used in the present study. This was done by two methods. In the first,¹⁰ a double-crystal spectrometer was used in the (1, -1) configuration with Cu $K\alpha$ radiation. The cleavage edge of a small calcite crystal about $4 \times 4 \times 10$ mm was set as the second crystal

TABLE II. Experimental values of density and grating constant d'_g at 25°C (based on $\lambda_{Cu K\alpha_1} = 1537.400$ xu and $\lambda_{Ag K\alpha_1} = 558.2594$ xu).

Crystal	Density (g/cm ³)	Grating Constants d' (xu)		
		d' (Cu $K\alpha_1$)	d' (Ag $K\alpha_1$)	d' (av)
1	2.710325	3029.566	3029.553	3029.560
2	2.709935		3029.638	3029.638
3	2.709974	3029.656	3029.669	3029.663
4	2.709905	3029.662	3029.669	3029.666
5	2.710091	3029.662	3029.649	3029.656
6	2.709865	3029.684	3029.691	3029.688
7	2.710112	3029.686	3029.694	3029.690
8	2.710156	3029.699	3029.694	3029.697
9	2.710000	3029.664	3029.674	3029.669

⁹ J. A. Bearden, A. Henins, J. G. Marzolf, W. C. Sauder, and John S. Thomsen, Phys. Rev. **135**, A899 (1964).

¹⁰ Albert Henins, Bull. Am. Phys. Soc. **9**, 387 (1964).

TABLE III. Experimentally measured dihedral angles with computed values for rhombohedral angle and geometrical volume factor Φ (all at 25°C).

Crystal	α (25°C)	β	Φ
1	105°03'20.2''	101°53'58.2''	1.095905
4	105°03'16.9''	101°53'56.2''	1.095894
5	105°03'16.5''	101°53'55.9''	1.095892
7	105°03'14.6''	101°53'54.7''	1.095886
9	105°03'15.8''	101°53'55.5''	1.095890
Average (excluding 1)			1.095891

with the edge parallel to and on the axis of the spectrometer. The angle α was measured by rotating the crystal to reflect from the two cleavage faces. In the second and more precise method, the W $K\alpha$ radiation was used and the second small crystal above adjusted for the (2, -2) in transmission. This has two advantages: Edge inhomogeneities are avoided, and the (2, -2) reflection is less than 2 sec in width, compared to more than 10 sec in the first method. The results from both methods were in reasonable agreement, but the latter have been used in the present computations.

The results are given in Table III. The adopted average, the mean of the last four values, is 1.095891 \pm 0.000005 at 25°C (equivalent to 1.095978 at 20°C). Individual values for the four samples lay within about 4 ppm of this average. The value obtained with No. 1, the Mexican crystal, was not included, since this sample was known to be of poor quality. Actually this result differed from the adopted one by about 15 ppm, still a comparatively low figure; this discrepancy was considered in assigning the probable error quoted above. Temperature corrections were made in each case; but since all measurements were obtained within $\pm 0.3^\circ\text{C}$ of 25°C, these were almost negligible.

Ideally, Φ should be determined for every crystal sample, along with its individual grating constant and density. There are two reasons why this procedure was not carried out. First, as noted above, small samples were required, necessitating undesirable damage to the original crystals. Secondly, as indicated above, the extreme range of variation of Φ is less than 20 ppm. On the other hand, the extreme range in the grating constant d' is over 40 ppm, and this quantity is cubed in Eqs. (1) and (2). Hence the effect of the variation of d' is much greater than that in Φ .

The small variation in Φ is probably not too surprising. If the ideal crystal had an orthogonal set of axes, then by symmetry these axes should remain orthogonal, on the average, when a small impurity content is present. The calcite axes are, of course, not orthogonal, but the rhombohedral angles do lie within about 12° of a right angle. Hence it seems plausible that the geometrical factor should be relatively insensitive to impurities.

F. Molecular Weight

The molecular weight of calcite can be computed from the atomic weights of calcium, carbon, and oxygen. The

TABLE IV. Experimental results for $\rho d'^3$ at 25°C and data for linearized equations. Origin value y_0 is taken as 7.536000×10^{10} .

Crystal	$y = \rho d'^3$ (g xu ³ /cm ³)	x_1	x_2	x_3	z
1	7.536332×10^{10}	40	300	40	44.0
2	7.535830×10^{10}	60	150	20	-22.6
3	7.536125×10^{10}	0	70	50	16.6
4	7.535955×10^{10}	0	40	10	-6.0
5	7.536398×10^{10}	30	50	160	52.8
6	7.536008×10^{10}	0	20	15	1.1
7	7.536710×10^{10}	0	60	200	94.2
8	7.536884×10^{10}	0	80	150	117.3
9	7.536242×10^{10}	0	60	150	32.1

last two are known to ample accuracy for the present purpose, and are 12.01115 and 15.9994, respectively.¹¹ The atomic weight of calcium is more uncertain. Chemical determinations¹² have given values of 40.082 and 40.083. It may also be computed from knowledge of the nuclidic masses and isotopic abundances. Using the abundances recommended by Nier, which are substantially the mean of the three sets listed in the table by Fuller,¹³ a value of 40.078 results. The value recently adopted by the Commission on Atomic Weights¹¹ was 40.08 (all figures quoted here are on the new C¹² scale). If the value 40.078 is used, the resulting molecular weight for calcite is 100.0874. To give some consideration to the higher chemical values, this will be rounded off to 100.088 ± 0.002 for the present investigation. The probable error assigned is based principally on the variations in reported isotopic abundances in calcite.

III. ANALYSIS

A. Extrapolation

Data from Tables I and II are summarized in Table IV, where

$$y = \rho d'^3, \quad (8)$$

and the impurity values (denoted by x 's) indicate ppm by *weight*, with

$$x_1 = x_{Mg}, \quad x_2 = x_{Mn}, \quad x_3 = x_{Sr}. \quad (9)$$

Other impurities of the order of a few parts per million are neglected, as before.

For the purpose of extrapolation it is now assumed that, when the impurity content is small, y is a linear function of the x 's i.e.,

$$y = Y \left(1 + \sum_{i=1}^3 a_i x_i \right), \quad (10)$$

where Y is the value of $\rho d'^3$ for a hypothetical crystal with zero impurities. It is convenient to rewrite this

relation in terms of a so-called "origin value" y_0 , which is close to the true value of Y . Subtracting this from both sides of the equation and then dividing by y_0 gives, to a high approximation,

$$Z + \sum_{i=1}^3 a_i x_i = z, \quad (11)$$

where the x_i 's are now in ppm and

$$z = 10^6(y - y_0)/y_0, \quad Z = 10^6(Y - y_0)/y_0. \quad (12)$$

In the present analysis, y_0 has been taken as 7.536×10^{10} ; values of z are indicated in the last column of Table IV. Each row of Table IV now represents an equation of the form of Eq. (11). For example, the first row may be written as

$$Z + 40a_1 + 300a_2 + 40a_3 = 44.0. \quad (13)$$

B. Least-Squares Analysis

The data in Table IV represent a set of 9 linear equations for 4 unknown quantities, *viz.*, Z , a_1 , a_2 , and a_3 . The most straightforward method of treating such an overdetermined set symmetrically is a least-squares adjustment (for details on this technique, see, for example, Bearden and Thomsen,¹⁴ or Cohen, Crowe and DuMond¹⁵).

At this point it is necessary to decide whether or not to assign unequal weights to these nine equations. Measurements of densities and grating constants are of comparable accuracy in every case. Since the error in impurity content is stated as a percentage of the reported impurity, crystals with high impurity content represent points of greater uncertainty in the adjustment. The effect of this factor on the error to be assigned to z cannot properly be determined until a preliminary adjustment has been carried out to obtain the approximate values of the a 's. It is then possible to assign a reasonably accurate set of weights and repeat the analysis. When this procedure was carried out in preliminary studies, the second solution differed only trivially from the first. Hence, in the present analysis the simplest procedure will be adopted and all equations assigned an equal weight.

The error to be associated with unit weight is not essential in evaluating the unknowns but is needed to perform a χ^2 test on the results. The *relative* probable error in ρ is about 1 ppm, and that in d' about 2 ppm, thus giving approximately 6 ppm in $\rho d'^3$. In addition, the uncertainty of $\pm 25\%$ in the various impurity values adds to the uncertainty in z . However, as mentioned above, this factor can not be properly evaluated until the coefficients a_i are known; even then it would pro-

¹¹ A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.* **84**, 4175 (1962).

¹² O. Hönigschmid and K. Kempter, *Z. Anorg. Allgem. Chem.* **195**, 1 (1931).

¹³ 1959 *Nuclear Data Tables*, edited by K. Way (U. S. Atomic Energy Commission, 1959), Table V.

¹⁴ J. A. Bearden and J. S. Thomsen, *Nuovo Cimento Suppl.* **5**, 267 (1957), App. B and Sec. C.

¹⁵ E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, *The Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957), Chap. 7.

duce unequal weights. Here, the *probable errors* in the various values of y are taken somewhat arbitrarily as 10 ppm, thus implying *standard deviations* of 15 ppm. Final *probable errors* are computed below on the basis of external consistency.

The normal equations are now obtained by the standard least-squares procedure. These are shown in Table V.

TABLE V. Normal equations for least-squares adjustment.

$9Z +$	$130a_1 +$	$820a_2 +$	$795a_3 =$	329.5
$130Z +$	$6100a_1 +$	$22\ 500a_2 +$	$7600a_3 =$	1988.0
$830Z +$	$22\ 500a_1 +$	$135\ 500a_2 +$	$60\ 200a_3 =$	30\ 356.0
$795Z +$	$7600a_1 +$	$60\ 200a_2 +$	$115\ 425a_3 =$	51\ 792.5

C. Results

The solution values for the normal equations are listed in Table VI, along with the resulting value of Y as given by Eq. (12).

Errors based on internal consistency (i.e., implied by the 10-ppm probable errors assigned to each of the input values) are obtained directly from the inverse matrix of the normal equations in Table V. This estimate may here be checked through use of the standard χ^2 test. The expected value $\langle \chi^2 \rangle$ is simply the number of equations minus the number of unknowns, i.e., $\langle \chi^2 \rangle = 9 - 4 = 5$, while the calculated value is $\chi^2 = 14.86$. Hence the originally estimated errors are evidently too low and must be increased by the factor $(14.86/5)^{1/2} = 1.72$ to obtain the errors on the basis of external consistency. Those errors are listed in Table VI.

It should be noted that almost the entire contribution to χ^2 comes from Crystals No. 8 and No. 9. If these were omitted, a new adjustment would give a value of Y with substantially lower error. However, the more conservative course has been adopted and the first adjustment retained.

Combining Eqs. (8) and (10) with the values from Table VI and converting from centimeters to milliangstroms now yields the result

$$\rho d'^3 = (7.53585 \pm 0.00009) \{ 1 - (0.85 \pm 0.36)x_1 + (0.26 \pm 0.09)x_2 + (0.51 \pm 0.08)x_3 \} \times 10^{-23} \text{ g(xu/m}\mathring{\text{A}})^3. \quad (14)$$

The error quoted for y in the above equation is purely statistical. When combined with estimated systematic probable errors of 3 ppm in ρ and 2 ppm in the average d' (6 ppm in d'^3), the resulting error is 15 ppm.

The value of $\rho d'^3$ for a hypothetical crystal of pure calcite is, of course, obtained by setting all of the x 's equal to zero. This result may now be substituted into Eq. (2) along with the values of Φ and M from Secs. II.E and II.F ($f = \frac{1}{2}$ for the rhombohedral cell of the calcite crystal). It follows that

$$N\Lambda^3 = (6.05972 \pm 0.00015) \times 10^{23} \text{ (g mole)}^{-1} \text{ (m}\mathring{\text{A}}/\text{xu})^3. \quad (15)$$

TABLE VI. Solution value, errors (by internal and external consistency), and χ^2 test.

Variable	Value	(P.E.) _{int}	(P.E.) _{ext}
Z	-20.05_4	7.33	12.6
a_1	-0.84_5	0.209	0.36
a_2	0.26_3	0.055	0.09
a_3	0.50_5	0.049	0.08
$Y = 7.535\ 849 \times 10^{10}$			
$\chi^2 = 14.86$			
$\langle \chi^2 \rangle = 9 - 4 = 5$			
$\frac{(\text{P.E.})_{\text{ext}}}{(\text{P.E.})_{\text{int}}} = \left[\frac{\chi^2}{\langle \chi^2 \rangle} \right]^{1/2} = \left(\frac{14.86}{5} \right)^{1/2} = 1.72_4$			

Combining this with the value of N recently recommended by the Committee on Fundamental Constants¹⁶ on the basis of an evaluation by Cohen and DuMond¹⁷ now gives

$$\Lambda = (1.002055 \pm 0.000009) \text{ (m}\mathring{\text{A}}/\text{xu}). \quad (16)$$

The various errors contributing to these two results are summarized in Table VII.

The above calculation has been made by extrapolating from the experimental values of $\rho d'^3$ to the "true" value for an ideal crystal; the correction required for any specific case is given by the term in parentheses in Eq. (14). It is equally possible to retain the experimental result for $\rho d'^3$ and to revise the true molecular weight to an effective value for a specific crystal, as done by Birge³ and Brogren.⁵ [In other words, for an impurity heavier than calcium, the true value of N may be obtained from Eq. (1) either by decreasing $\rho d'^3$ or increasing M .] The same correction term must then appear in the numerator, giving

$$M_{\text{eff}} = M \left[1 + \sum_{i=1}^3 a_i x_i \right]. \quad (17)$$

This may now be compared with Eq. (3).

Since X_i in the latter represents the ratio of impurity

TABLE VII. Errors contributing to final results.

Source	Error (ppm)	
$\rho d'^3$ (statistical)	13	
ρ (systematic)	3	
d'^3 (systematic: 3×2 ppm)	6	
A	20	
Φ	5	
N	rms error in $N\Lambda^3$	25
		10
	rms error in Λ^3	27
	rms error in Λ	9

¹⁶ Committee on Fundamental Constants of the National Academy of Sciences, Phys. Today 17, 48 (February, 1964).

¹⁷ E. R. Cohen and J. W. M. DuMond, in *Proceedings of the Second International Conference on Nuclidic Masses and Atomic Constants, Vienna, 1963* (Springer-Verlag, Berlin, to be published).

TABLE VIII. Experimental and theoretically calculated values for coefficients in Eq. (10). Molecular weights for calcium and calcite are taken as 40.078 and 100.088, respectively.

<i>i</i>	Impurity	Molecular weight M_i	Experimental a_i	Theoretical a_i	
				Substitutional	Interstitial
1	Mg	24.312	-0.85 ± 0.36	-0.65	+1.00
2	Mn	54.9380	$+0.26 \pm 0.09$	+0.27	+1.00
3	Sr	87.62	$+0.51 \pm 0.08$	+0.54	+1.00

atoms to calcium atoms, the weight ratio of impurity to total crystal, x_i , is approximately $x_i = X_i M_i / M$. Comparison of Eqs. (3) and (17) then shows

$$a_i = \Delta M / M_i. \quad (18)$$

Theoretical values of the a_i 's may now be easily calculated with the help of Eqs. (4) and (5) for the substitutional and interstitial cases, respectively; in the latter case, all a_i 's will be equal to unity.

Table VIII shows a comparison of the experimental and calculated values of the a_i 's. In all cases, the calculated substitutional values lie within the error range (probably indicating that the errors assigned by external consistency are somewhat high), while the calculated interstitial values differ by at least 5 probable errors. These results indicate rather conclusively that the impurities are primarily substitutional in form.

This confirms the basis of correction used by Birge³ and Brogren.⁵ It would appear, as suggested by Brogren, that the impurity analysis of the crystals previously used by Bearden⁴ did not include strontium; hence Birge's correction based on these data was evidently too small.

IV. ADOPTED VALUE FOR Λ

Evaluation of the conversion factor $\Lambda = \lambda_g / \lambda_s$ has been extensively discussed in a recent paper by Henins

and Bearden.² The original program for obtaining a more precise value of Λ included an extensive series of ruled grating measurements, performed simultaneously with the present study. However, various unforeseen difficulties developed, which have thus far prevented successful completion of this grating experiment. Hence it has been necessary to rely primarily on less direct, but more precise methods, such as the present study.

Table IX summarizes the presently available high-precision data on Λ ; it is essentially Table VII of the Henins and Bearden² paper with the addition of the present result. Minor changes in the various values and errors as evaluated by these authors include: The result of the Spijkerman " h/e experiment" (Item 1) has been stated to one additional figure and a slight correction made in the corresponding error computed for Λ . The probable error estimate in the Smakula result (Item 5) has been lowered from 25 to 15 ppm. This figure is principally dependent on a possible systematic error common to all of his x-ray measurements (due to such factors as centering and instrumental window corrections); it can not be determined statistically and is difficult to estimate in an objective way. The error for the various crystals with the Mo $K\alpha_1$ radiation (Item 6) has been lowered from 25 to 20 ppm. Again, statistical treatment would indicate a still lower figure; however, the situation is complicated by the prior rejection of some results and by serious correlations among the data actually used.

Most of the experiments shown in Table IX (all except Item 6) were performed either with Cu $K\alpha_1$ radiation or other lines in the same wavelength region. In these experiments, the wavelength value of the Cu $K\alpha_1$ line was usually taken as approximately 1537.40 xu. Hence, for historical reasons, the values of Λ are listed on this basis in the second column of Table IX. However, on the basis of 208.5770 xu for the W $K\alpha_1$ line, the value stated in the recent determination of

TABLE IX. Comparative values of Λ from different experimental sources and recommended mean. Atomic constants needed in calculation of these values of Λ are taken from those recommended by the Committee on Fundamental Constants (Refs. 16 and 17).

Experiment	Value (Cu $K\alpha_1 = 1.537400$)	Λ Value (W $K\alpha_1 = 208.5770$)	Error (ppm)	Second weighting
1. Spijkerman ^a gas target " h/e expt."	1.002008	1.002028	26	1
2. Bearden ^b plane ruled grating	1.002030	1.002050	30	1
<i>Crystal density and grating constants:</i>				
3. Henins ^c (Si)	1.002057	1.002077	5	10
4. Bearden ^d (CaCO ₃)	1.002055	1.002075	9	3
5. Smakula ^e (7 crystals)	1.00207	1.00209	15	2.5
6. Various ^f Mo $K\alpha_1$ values (CaCO ₃ , quartz, diamond)	1.00205	1.00207	20	1
<i>Mean values:</i>				
Statistical weighting	1.002056	1.002076	{ 4 (internal consistency) 3 (external consistency)	
Second weighting	1.002054	1.002074	4 (external consistency)	

^a J. J. Spijkerman and J. A. Bearden, Phys. Rev. **134**, A871 (1964).

^b J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

^c I. Henins and J. A. Bearden, Phys. Rev. **135**, A890 (1964).

^d Present paper.

^e A. Smakula and T. Kalnajs, Nuovo Cimento Suppl. **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); see also Ref. c.

reference wavelengths by Bearden *et al.*,⁹ the Cu $K\alpha_1$ figure must be lowered by 20 ppm. The third column of Table IX shows the corresponding values of Λ with this alteration. The next column gives probable errors of the various experiments, *as estimated by the present author*.

Two different weighted averages were formed. In the first case, the usual statistical procedure was followed, with weights taken as proportional to the inverse square of the errors. In the second averaging, weights were assigned somewhat arbitrarily, as shown in the last column; these gave slightly more emphasis to the less accurate data. It is evident that the resulting weighted average is insensitive to this change. Consistency of the data is quite good, in light of the assigned errors; the error of the mean based on external consistency is somewhat smaller than that obtained by internal consistency (i.e., χ^2 is lower than its expected value).

It was noted that adoption of the first average, $\Lambda = 1.002076$ (*in the third column*), would give the W $K\alpha_1$ line a value of 0.2090100 Å. Since it thus yields a convenient value to use for a standard reference line and lies well within the probable error of the second average, it was decided to adopt this figure and increase the assigned *probable error* to 5 ppm. Hence the final recommended value (based on $\lambda_{\text{Cu } K\alpha_1} = 1537.400$ xu) is

$$\Lambda = 1.002056 \pm 0.000005 \text{ mÅ/xu}. \quad (19)$$

Recently, it has been learned that Edlén and Svensson¹⁸ have reexamined the plates used with the Al $K\alpha_{1,2}$ lines in Tyrén's¹⁹ excellent concave grating experiment. They have now applied necessary Lamb shift corrections and obtained a revised value of Λ from the Tyrén work. This appears to be consistent, within their stated error, with that given above. However, there is some uncertainty as to the exact value of the Al $K\alpha_{1,2}$ wavelength in x units. Further discussion of this work before publication seems premature.

V. CONCLUSIONS

(1) An experimental relation has been obtained for calcite, giving the product $\rho d'^3$ as a function of the principal impurities in the crystal. This is presented in Eq. (14). The results indicate that the impurities are primarily substitutional in form.

¹⁸ B. Edlén and L. A. Svensson (private communication).
¹⁹ F. Tyrén, *Nova Acta Regiae Soc. Sci. Upsalensis* **12** N. 1 (1940).

(2) The error in the product $\rho d'^3$ is primarily due to that in the atomic weight of calcium. A more precise determination of the nuclidic abundances of this element would permit better use of the present experimental results.

(3) When combined with other available data on Φ (measured in this laboratory), the atomic weight M and Avogadro's number N , this result yields

$$N\Lambda^3 = (6.05972 \pm 0.00015) \times 10^{23} (\text{g-mole})^{-1} (\text{mÅ/xu})^3. \quad (15)$$

(4) The value of Λ obtained in this experiment, along with those from prior determinations, as discussed at length by Henins and Bearden,² are summarized in Table IX. A weighted average has been taken as shown, giving a value of

$$\Lambda = (1.002056 \pm 0.000005) \text{ mÅ/xu}. \quad (19)$$

Both Eqs. (15) and (19) are based on an x-unit scale such that $\lambda_{\text{Cu } K\alpha_1} = 1537.400$ xu.

(5) In the redetermination of reference wavelengths by Bearden *et al.*,⁹ the value for the W $K\alpha_1$ line is given as 208.5770 xu, and the Cu $K\alpha_1$ value quoted above is lowered by 20 ppm. In a forthcoming wavelength table edited by the author, the W $K\alpha_1$ line has been adopted as the standard reference line and the above-quoted value in x units has been used in preparing a working table of wavelengths. On this basis, Λ must be raised 20 ppm and becomes

$$\Lambda = (1.002076 \pm 0.000005) \text{ mÅ/xu}. \quad (20)$$

With either convention for the x-unit scale, the wavelength value in absolute units is

$$\lambda_{\text{W } K\alpha_1} = 0.2090100 \text{ Å}. \quad (21)$$

This last figure has been adopted as defining *the standard wavelength* on which the entire table is based.

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