

the bent quartz crystal, is thinned down by light etching until we have relatively few lines in our imperfect grating: the net result being that the doubled lines are un-resolved and even blurred (see Fig. 3(b), reference 5) by the scanty grating available.

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The Fundamental Relation Between Lattice Constants and Density*

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Lattice constants have for many years been based on Siegbahn's crystal wave-lengths which are now known to be different from true wave-lengths. It is proposed that a unit called the "crystal angstrom" be defined as follows: 1 crystal angstrom = $1A_{cr} = 10^8 X$ units, and be used in crystal structure work where "crystal wave-lengths" are used. $1A_{cr}$ is not equal to 10^{-8} cm. To place the calculation of the density from lattice constant measurements on a sound and uniform basis it is proposed that the fundamental density equation be rewritten in the form $\rho = K(nM/V')$ where n = No. of atoms or molecules in the unit cell, M = atomic or molecular weight and V' = volume of the unit cell in crystal angstroms. The constant K is evaluated empirically from data on calcite and is found to be equal to $1.650_{23} \pm 0.00015$ where 0.00015 is the calculated value of the standard deviation. This is the only value which is consistent with (1) the basis for the crystal wave-

length scale adopted by Siegbahn, namely $d_{100} = 3.02945 A_{cr} = 3029.45 X$ units at $18^\circ C$ for the cleavage cell of calcite, and (2) the best available values for the atomic weight, density and rhombohedral angle of calcite. This value of K must be used in calculating densities from lattice constants if crystal wave-lengths are used. Density calculations are made for five metals and compared with directly measured densities. The error in the calculated density attributable to errors in lattice constant measurements is generally smaller than those due to the atomic weights and to K . For Al, Mg and Ni excellent agreement is obtained between the calculated and measured densities. For Cu and Ag there is marked disagreement but since the directly measured densities are far from concordant while the lattice constants of various investigators agree closely, it is concluded that the main source of the discrepancy lies in the directly measured values.

FOR many years, the scale of wave-lengths for x-rays proposed by Siegbahn and the relative wave-lengths tabulated by him have been the basis for the evaluation of lattice constants. Densities calculated from such lattice constant data have frequently not agreed well with directly measured densities and much speculation has arisen as to the reason for the disagreement. Fundamentally, the Siegbahn wave-length scale may be considered to be based on the measured density of calcite. This may be seen from the agreement between the calculated and measured calcite spacings which Siegbahn¹ himself dis-

cussed and considered as fortuitous. It seems unnecessary to enter into the detailed arguments at this point as to why calcite turns out to be the ultimate standard rather than sodium chloride. As far as density calculations are concerned we may state simply that if the value for Avogadro's number used by Siegbahn ($N = 6.0594 \times 10^{23}$) had been used consistently in subsequent calculations of density from lattice constants based on the Siegbahn wave-length scale, the accuracy of densities would have been limited only by (1) the accuracy of the density and rhombohedral angle values of calcite used by Siegbahn, (2) the accuracy of the determinations of the lattice constants and (3) the relative accuracy of the molecular weight of calcite compared with that of

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¹M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Springer, Berlin, 2nd Ed., 1931).

the substance being considered. In recent years, new determinations of Avogadro's number have been made, the relation between the Siegbahn wave-length scale and the absolute scale has been investigated,* and new experimental data on other fundamental values involved in calculating the calcite spacing have been available. These changes have obvious bearing on density calculations.

The main objectives of this article are: (1) To indicate a way by which immediate decision on the choice of the wave-length scale and on the true value of Avogadro's number becomes unnecessary. (2) To put the calculation of density from lattice constants on as thoroughly sound a basis as the experimental data available at present will permit. (3) To demonstrate that the main source of discrepancy between densities calculated from lattice constants and directly measured densities does not lie in lack of precision in determining lattice constants.

In order to minimize the confusion which is certain to arise until there is a general agreement to use absolute wave-lengths rather than crystal

* Concerning the use of absolute wave-lengths, we shall not attempt to answer the question of whether in the long run it would be better to retain the Siegbahn scale for crystal structure work, making the conversions to the absolute scale for those few problems where it is important, or to recalculate more than 25 years of crystal structure determinations to the absolute scale.

wave-lengths, we propose the adoption of a unit which we shall call the "crystal angstrom," a term suggestive of "crystal wave-lengths," and which we shall define by the equation:

$$1 \text{ crystal angstrom} = 1A_{\text{cr}} = 10^3 (X \text{ units}).$$

This unit would apply to all measurements made in terms of Siegbahn's crystal wave-lengths. If we represent "absolute angstroms" by A and define the ratio

$$f = \frac{(\text{wave-length in centimeters})}{(\text{wave-length in } X \text{ units}) \times 10^{-11}},$$

we may also write our definition of the "crystal angstrom" in the form

$$1 \text{ cm} = 10^8 A = \frac{10^8}{f} A_{\text{cr}} = \frac{10^{11}}{f} (X \text{ units}).$$

It is to be emphasized that all previously reported lattice constants have actually been given in crystal angstroms and not in centimeters $\times 10^{-8}$.

The fundamental relation used for calculating densities from x-ray measurements is

$$\rho = \frac{\text{mass}}{\text{vol.}} = \frac{nM}{N} \frac{1}{V}, \quad (1)$$

TABLE I. Values of the density of calcite.

AUTHOR	ORIGIN	T	ρ	PROB. ERROR	ρ_{18}
Defoe and Compton ¹	Missouri	0°	2.7114	0.0001	2.7107
	U.S.A.	0°	2.7110	0.0001	2.7103
	Iceland	0°	2.7111	0.0001	2.7104
	Iceland	0°	2.7098	0.0001	2.7091
	Unknown	0°	2.7109	0.0001	2.7102
Bearden ²	Unknown	0°	2.7112	0.0001	2.7105
	Iceland	20°	2.7104	0.00002	2.7105
	Iceland	20°	2.71035	0.00002	2.71043
	Montana	20°	2.7102	0.00008	2.7103
	Montana	20°	2.7102	0.00002	2.7103
Tu ³	Argentina	20°	2.7102	0.00004	2.7103
	Spain	20°	2.7102	0.00004	2.7103
	Unknown	18°	2.71003	0.00005	2.71003
DuMond and Bollman ⁴	Unknown, powdered	20°(?)	2.71022	0.00035	2.71030
	Macroscopic	20°(?)	2.71085	0.00019	2.71093
Batuecas and Casado ⁵	Unknown, powder, 1.2 mm	0°	2.71123	0.00011	2.71055

Stand. Dev. = $\Delta\rho = [\Sigma(v_i)^2/n(n-1)]^{1/2} = 9.7 \times 10^{-5}$; Av. $\rho_{18} = 2.71032 \pm 0.00010$.

¹ O. K. Defoe and A. H. Compton, Phys. Rev. 25, 618 (1925).

² J. A. Bearden, Phys. Rev. 38, 2089 (1931); 48, 385 (1935).

³ Y. C. Tu, Phys. Rev. 40, 662 (1932).

⁴ J. W. M. DuMond and V. L. Bollman, Phys. Rev. 50, 524 (1936).

⁵ T. Batuecas and F. L. Casado, Zeits. f. physik. Chemie 181A, 197 (1937).

TABLE II. Values of the dihedral angle of calcite; calculation of $\phi(\beta)$.

AUTHOR ¹	ORIGIN	T	α	α_{18}
Bearden	Iceland	20°	105° 3' 29''	105° 3' 39''
	Montana	20°	105° 3' 31''	105° 3' 41''
	Argentina	20°	105° 3' 28''	105° 3' 38''
	Spain	20°	105° 3' 29''	105° 3' 39''
Tu	Unknown	18°		105° 3' 23.7''
DuMond and Bollman	Unknown	Recalculated by authors		105° 3' 34''
Stand. Dev. = $\Delta\alpha = \pm 2.6''$				Av. $\alpha_{18} = 105^\circ 3' 35.8'' \pm 2.6''$
$\beta_{18} = 101^\circ 54' 7.7'' \pm 1.6''$; Av. at 18°C $\phi(\beta) = \frac{(1 + \cos \beta)^2}{(1 + 2 \cos \beta) \cdot (1 - \cos^2 \beta)^{\frac{1}{2}}} = 1.095956 \pm 0.0000093$.				

¹ See references to authors given in Table I.

where n = No. of atoms (or molecules) in the unit cell, M = atomic (or molecular) weight in grams, N = Avogadro's number—No. atoms in gram atomic weight or the corresponding molecular quantity—and V = true volume of unit cell in cubic centimeters.

In order to retain the Siegbahn scale, we shall write Eq. (1) in the form

$$\rho = nM \cdot 10^{24} / f^3 N V', \quad (2)$$

where V' = volume in crystal angstroms. We propose that at present the values of both f and N be considered as not fully established and that Eq. (2) be modified to

$$\rho = K n M / V', \quad (3)$$

where

$$K = 10^{24} / f^3 N. \quad (4)$$

The value of K can be obtained directly from (4). It may also be found empirically from suitable data by means of (3). For the present it seems best to resort to the latter alternative using data for the reference substance on which the crystal wave-length scale itself is based, namely calcite. The required values have been determined repeatedly by various investigators with, generally, excellent agreement.

The experimental values of the density of calcite are given in Table I which includes the value originally reported, the value corrected to 18°C by means of Benoit's² data on the expansion coefficients, and the probable errors of the determinations given by the original investigators. The number of significant figures for each value in these tables is the same as that given in the

original source. It is important to notice that in each case where an investigator used different samples of calcite for the measurements, the range or "spread" of the values is well beyond the stated probable errors.

The three factors which can give rise to density differences among the several calcites are (1) differences in chemical composition, (2) differences in physical imperfections, voids, fissures, inclusions, lattice irregularities, etc., and (3) the presence of systematic errors in the determinations. Bearden³ is the only one to report chemical analyses; the results were closely similar showing about 99.98 mol. percent CaCO_3 . Nothing is known concerning the other two factors but it cannot be assumed that the samples were all identical with respect to the second or that the systematic errors were the same for all investigators. We shall, therefore, treat each value given in Table I as an individual value. The character of the information available also makes it necessary to give equal weights to all the values. At the bottom of Table I we give the mean value of ρ and the standard deviation of the listed values, calculated as indicated.

Calculation of the density of calcite is usually made in terms of the cleavage rhombohedron for which $\phi(\beta)$ is a function of the characteristic rhombohedral angle β and d_{100} is the spacing of the cleavage cell. In terms of crystal angstroms we have $V' = \phi(\beta) \cdot d_{100}^3$. The angle usually measured is the dihedral angle α which is related to β by the equation $\cos \frac{1}{2}\beta = 1 / (2 \sin \frac{1}{2}\alpha)$. The measured values of α are given in Table II, together with the values calculated to 18° which again

² Benoit, Int. Crit. Tab. III, 44.

³ J. A. Bearden, Phys. Rev. **38**, 2089 (1931); **48**, 385 (1935).

involve Benoit's data on expansion coefficients.⁴ As in the case of the density data, each value in Table II was considered as an individual determination and given the same weight. Again the *standard deviation* of the listed values of α is given. At the bottom of the table the calculated values of β and $\phi(\beta)$ with their respective *standard deviations* are given.

For the molecular weight of CaCO_3 several different estimates are possible. We have adopted the value suggested by Birge⁵ but have multiplied the probable error of 0.0054 by 1.5 to secure the standard deviations. The value on the chemical scale is $M = 100.09_0 \pm 0.0081$.

For d_{100} we use the arbitrary value adopted by Siegbahn as the basis of the crystal wave-length scale $d_{100} = 3.02945A_{\text{cr}}$ at 18°C .

In Table III we give the value of K calculated from the preceding data and Eq. (3).

This value of K is the only one consistent with the measured density and crystallographic data on calcite and the adopted basis of the crystal wave-lengths used in lattice constant measurements. It is, therefore, this value of K which

TABLE III. Calculation of K .

$n = 0.5$	
$M = 100.09_0 \pm 0.0081$	$\Delta M/M = 8.1 \times 10^{-5}$
$\rho = 2.710_{32} \pm 0.00010$	$\Delta\rho/\rho = 3.7 \times 10^{-5}$
$d_{100} = 3.02945$	$\Delta d/d = 0$ (reference length)
$\phi(\beta) = 1.09595_6 \pm 0.0000093$	$\Delta\phi(\beta)/\phi(\beta) = 0.8 \times 10^{-5}$
$K = \frac{\rho d_{100}^3 \phi(\beta)}{nM} = 1.65023$	
$\frac{\Delta K}{K} = \pm \left[\left(\frac{\Delta\rho}{\rho} \right)^2 + \left(\frac{\Delta\phi(\beta)}{\phi(\beta)} \right)^2 + \left(\frac{\Delta M}{M} \right)^2 \right]^{\frac{1}{2}} = 8.94 \times 10^{-5}$	(cf. Eq. (6))
Stand. Dev. = $\Delta K = 14.7 \times 10^{-5}$, $K = 1.650_{23} \pm 0.00015$.	

⁴ Of Bearden's results (reference 3) the values from his methods 1 and 2 were used and the mean for each calcite is given in Table II. Bearden also discarded the results of his third method. The x-ray results of DuMond and Bollman (reference 4, Table I) were subject to a considerable systematic error which we were able to eliminate by methods previously used in this laboratory (reference 7). These authors unfortunately do not state the temperature at which any of their measurements were made; from internal evidence it was inferred that the results were reported at 20°C . The results of Beets (H. N. Beets, Phys. Rev. 25, 621 (1925)) seemed definitely too high by about 90 seconds in comparison with those of three later investigations and have been omitted entirely.

⁵ R. T. Birge, "A consistent set of values of the general physical constants." Mimeographed letter, August 1939, page 5.

must be used in calculating densities from lattice constants so long as (1) the Siegbahn crystal wave-lengths are used, (2) the molecular weight of calcium carbonate is unchanged and (3) no better values for the density and $\phi(\beta)$ of calcite are available.* It must be emphasized that for any comparison of the calculated densities with directly measured values to be valid, *the material which is used for the direct measurement must enable the investigator to obtain the true density rather than the apparent density and must have the same composition as the solid phase to which the lattice constant determinations apply*. These requirements go far deeper than might at first be supposed. The direct density measurements are influenced by cracks, holes, solid or liquid inclusion, surface films of oxides or adsorbed gas, etc., which do not influence the lattice constant determinations at all. Both types of method of measuring densities are affected by internal strain such as arises from cold work or quenching. Finally, the interpretation of any density, however measured, is dependent upon the chemical analysis of the material and this is particularly important in the case of the x-ray methods where the mass per unit cell must be computed with the aid of the analysis of the particular solid phase under investigation.

Following the conventional methods used by physicists in computing errors, the standard deviations of K in Table III and of V' and ρ in Table IV have been obtained by means of the equation⁶

$$(\Delta c)^2 = (\partial c/\partial x)^2 \langle \Delta x \rangle_w^2 + (\partial c/\partial y)^2 \langle \Delta y \rangle_w^2 + \dots \quad (5)$$

For the constant K in Table III this becomes

$$\Delta K/K = \pm \left[(\Delta\rho/\rho)^2 + (\Delta\phi(\beta)/\phi(\beta))^2 + (\Delta M/M)^2 \right]^{\frac{1}{2}} \quad (6)$$

In calculating the densities in Table IV, we have used

$$\Delta\rho/\rho = \pm \left[(\Delta M/M)^2 + (\Delta K/K)^2 + (\Delta V'/V')^2 \right]^{\frac{1}{2}} \quad (7)$$

where $\Delta V'/V' = 3(\Delta a_0/a_0)$ for cubic crystals and

* The value of $10^{24}/K = 6.0598 \times 10^{23}$ is very close to the Avogadro number used by Siegbahn, reference 1.

⁶ R. T. Birge, Am. Phys. Teacher 7, 351 (1939).

TABLE IV. Calculation of ρ and $\Delta\rho$ from lattice constants ($T=25^\circ\text{C}$).

	Al	Mg	Ni	Cu	Ag
a_0	4.0413 ₉	(*)	3.5168 ₄	3.6077 ₈	4.0778 ₇
V'	66.00 ₇₄	46.20 ₂₅	43.49 ₆₉	46.95 ₉₁	67.81 ₁₀
M	26.97	24.32	58.69	63.57	107.880
K	1.650 ₂₃	1.650 ₂₃	1.650 ₂₃	1.650 ₂₃	1.650 ₂₃
n	4	2	4	4	4
ρ	2.69 ₇₁	1.737 ₃	8.90 ₆₅	8.93 ₅₈	10.50 ₁₃
Δa_0	0.00004	(*)	0.00004	0.00004	0.00004
$(\Delta V'/V') \times 10^5$	3.0	5.2	3.4	3.3	2.9
$(\Delta M/M) \times 10^5$	37.1	41.1	17.0	15.7	0.9
$(\Delta K/K) \times 10^5$ (Eq. (6))	8.9	8.9	8.9	8.9	8.9
$\Delta\rho/\rho \times 10^5$ (Eq. (7))	38.3	42.4	19.5	18.3	9.4
$\Delta\rho$	0.0010	0.0007	0.0017	0.0016	0.0010

* $a = 3.2030_0 \pm 0.00008$; $c = 5.2002_1 \pm 0.00007$.

$\Delta V'/V' = \pm [(2\Delta a/a)^2 + (\Delta c/c)^2]^{1/2}$ for hexagonal crystals.

We shall illustrate the application of Eq. (3) and the calculations of the errors with several specific cases. We should mention at this point that the important question regarding the necessity of applying a refraction correction in the calculation of lattice constants has not yet been finally decided. However, in only one of the cases to be discussed below does this correction reach a value which will sensibly affect the result. This case is silver and the omission of the correction increases the calculated density by about one or two parts in 10,000.

In Table IV we give the results of calculations of the densities for five metals. The lattice constants were taken from measurements made by the authors and all, except the value for copper have been previously reported.⁷ These values were corrected for refraction. For the standard deviation of the atomic weight we have assumed plus or minus one unit in the last significant figure quoted for the element in the 1939 table of "International Atomic Weights." This appears to be a safe assumption and one not likely to affect our main conclusions significantly. As will be seen, should the chosen standard deviation prove to be too large, the calculated densities would become even more reliable.

The values of $\Delta\rho/\rho$ in Table IV were found from Eq. (7). A study of these results shows that for these measurements the part of the error in the density attributable to errors in the lattice

constants are in every case much less than at least one of the other two errors. In only one case (Ag) is this error greater than that due to the uncertainty in the atomic weight. Since it is possible by modern methods for any competent investigator to obtain lattice constants with the same order of accuracy as those quoted, the main source of the discrepancy between the calculated and measured densities must be sought in the other quantities including, of course, the measured densities themselves.

In Table V we compare the calculated densities found in Table IV with densities directly measured by various investigators. It will be seen that the agreements in the cases of aluminum, magnesium and nickel are excellent. For copper and silver the situation is quite different. The calculated and measured densities show wide discrepancies. In an investigation in this laboratory with copper from four different sources, including a "spectroscopic" copper, with samples heat treated in various ways to yield a total of 16 different measurements, the lowest value of a_0 secured was 3.6076₃ and the highest 3.6081₅ A_{cr.} This range will include all the precision measurements on copper recently published and the "spread" of the density values calculated from such measurements will at the most be about ± 2 parts in 10,000, a trifle more than $\Delta\rho/\rho$ given in Table IV. The same degree of agreement is found for silver. The source of the disagreement in densities must, therefore, be sought either in the direct density measurements, or, what is the far more probable source, in the samples used in the direct measurements. In this connection we may mention the extensive work of Ruer and

⁷ E. R. Jette and F. Foote, J. Chem. Phys. **3**, 605 (1935). In this paper fiduciary limits with $P=0.05$ were used in reporting the errors. These have been converted to standard deviations in Table IV.

TABLE V. Comparison of calculated and measured densities at 25°C.

	ρ_{CALC}	ρ_{MEAS}	SOURCE OF ρ_{MEAS}
Al	2.6971±0.0010	2.6978 2.6967±0.0003	Taylor ¹ <i>et al.</i> Batuecas and Casado ²
Mg	1.7373±0.0007	1.7373±0.0002 1.738 1.736	Batuecas and Casado ² Elchardus ³ F. Foote (unpublished)
Ni	8.9065±0.0017	8.901-8.903	Jordan and Swanger ⁴
Cu	8.9358±0.0016	8.9154 8.94126 8.94304 8.95231 8.94±0.01	Ruer and Kuschmann ⁵ Maier, ⁶ vac. melted and solidified Maier, ⁶ vac. melted and solidified under He Maier, ⁶ single crystal Int. Crit. Tab. II, 456
Ag	10.5013±0.0010	10.4936 10.492 10.50 10.438-10.535 10.489	Ruer and Kuschmann ⁵ Jette and Foote ⁷ Phelps and Davey ⁸ Int. Crit. Tab. II, 456 Kahlbaum, ⁹ <i>et al.</i> (vac. distilled)

¹ C. S. Taylor, L. A. Willey, D. W. Smith and J. D. Edwards, *Metals and Alloys* **8**, 183 (1938).

² See reference 5, Table I.

³ E. Elchardus, Value reported by van Arkel, *Reine Metalle* (Springer, Berlin, 1939), p. 119.

⁴ L. Jordan and W. H. Swanger, *Bur. Stand. J. Research* **5**, 1291 (1930).

⁵ R. Ruer and J. Kuschmann, *Zeits. f. anorg. allgem. Chemie* **173**, 233,

262 (1928).

⁶ C. G. Maier, *Trans. Am. Inst. Min. Met. Eng.* **123**, 121 (1936).

⁷ See reference 7 in text.

⁸ R. T. Phelps and W. P. Davey, *Trans. Am. Inst. Min. Met. Eng.* **99**, 234 (1932).

⁹ G. W. A. Kahlbaum, K. Roth and P. Seider, *Zeits. f. anorg. allgem. Chemie* **29**, 177 (1902).

Kuschmann,⁸ who have shown the effects of chemical treatment and of annealing under various conditions upon the densities, and of Maier,⁹ who investigated the effects of various mechanical and heat treatments on the densities. The remarkably high value for a large single crystal of copper (cf. Table V) is entirely beyond the range of any normal errors and has not been explained.

It is interesting to calculate K from Eq. (4) with data given by Birge⁵ recognizing, of course, that Birge does not intend these values to be final ones.

$$N = (6.0227_4 \pm 0.0014) \times 10^{23}$$

$$\text{Stand. Dev.} = \Delta N = \pm 0.0021$$

⁸ R. Ruer and J. Kuschmann, *Zeit. f. anorg. allgem. Chemie* **173**, 233, 262 (1928).

⁹ C. G. Maier, *Trans. Am. Inst. Min. Met. Engrs.* **123**, 121 (1936).

$$f = 1.002034 \pm 0.00006$$

$$\text{Stand. Dev.} = \Delta f = \pm 0.00009.$$

From Eq. (4) we obtain

$$K = 10^{24}/f^3 N = 1.650_{28} \pm 0.00074,$$

where ΔK the standard deviation is obtained by means of

$$\Delta K/K = \pm [(3\Delta f/f)^2 + (\Delta N/N)^2]^{1/2} = \pm 0.00045.$$

A similar calculation but with Bearden's³ estimate that the probable error in f is 0.000016 with a corresponding standard deviation $\Delta f = 0.000024$ gives $K = 1.650_{28} \pm 0.00059$. When these values of K are compared with the one in Table III, it will be seen that the values differ by only 3 parts per 100,000 and the main difference lies in the standard deviations.