THE GRATING SPACE OF CALCITE AND ROCK SALT

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Abstract

Grating spaces of calcite and rock salt are recalculated using the new values for the crystal densities obtained by DeFoe and Compton, and come out for calcite 3.0291±.0010A and for rock salt, 2.8147±.0009A at 20°C. The values for each degree from 15° to 25° are given in a table. These values are slightly greater than those usually given. The remaining uncertainty is due chiefly to that in Avogadro's number. The ratio $D(CaCO_3)/D(NaCl)$ comes out 1.0762 ±.0002(18°C) which agrees satisfactorily with Siegbahn's value, 1.0764. The uncertainty in this value is chiefly associated with the molecular weights.

Absolute wave-length values corrected for refraction.—The correction is made by using an effective grating space slightly smaller than the true value. For the first order from calcite the effective value is 3.0287 and for rock salt 2.8144A, both at 20°C. Using these values the *wave-length of Mo* $K\alpha_1$ line is found (Siegbahn) to be .70749±.00023A.

According to Bragg's law the wave-length λ of a beam of x-rays reflected from a crystal at a glancing angle θ is given by

$$n\lambda = 2D\sin\theta, \qquad (1)$$

or more precisely by

$$n\lambda = 2D\sin\theta(1-\delta/\sin^2\theta), \qquad (2)$$

where n is the order of the spectrum, D is the grating space or distance between successive layers of atoms in the crystal grating, and $\delta = 1-\mu$, μ being the index of refraction of the x-rays in the crystal. At present it is possible to measure θ to a degree of accuracy such that by far the greater part of the error in determining the absolute wave-length of a beam of x-rays is due to the uncertainty of D. It is thus of obvious importance to determine this grating space with precision.

From very fundamental considerations of the principles underlying crystal structure, it can be shown that the grating space of a rhombohedral crystal is given by

$$D = (nM/\rho N\varphi(\beta))^{1/3}, \qquad (3)$$

where n is the number of molecules per elementary rhombohedron, M is the molecular weight, ρ the density, N the number of molecules per gram molecule, and $\varphi(\beta)$ is the volume of a rhombohedron the distance

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between whose opposite faces is unity and the angle between whose edges, β, is that between the axes of the crystal. For the two most commonly used crystals, rock salt and calcite, $n=1/2$, and M is known with rather high precision. For rock salt, $\beta=90°$, whence $\varphi(\beta)=1$; but for calcite the uncertainty of the value of β has been considered an appreciable source of error.[1] The density ρ does not appear to have been measured for either crystal with the care its importance would warrant, so that it also contributes appreciably to the probable error. In estimating D, the uncertainty of the value of N introduces the greatest single source of error, though no greater than that which Uhler estimates[1] as due to the combined error of ρ and β in the case of calcite.

By introducing the values of ρ and β which we have measured as described elsewhere in this journal, we are able to reduce somewhat the probable error of the calculation of the grating spaces of calcite and rock salt from Eq. (3). We have:

For calcite,	For rock salt,
$n=1/2$(2)	$n=1/2$(2)
$M=100.075\pm .03$(3)	$M=58.46\pm .02$(3)
$\rho=2.7102\pm .0004$ at 20°(4)	$\rho=2.1632\pm .0004$ at 20°(4)
$N=(6.0594\pm .006)\times 10^{23}$(5)	$N=(6.0594\pm .006)\times 10^{23}$(5)
$\varphi(\beta)=1.09630\pm .00007$ at 20°(6)	$\varphi(\beta)=1.$

Substituting these values in equation (3) we obtain

$$D(\mathrm{CaCO_3})=(3.0291\pm .0010)\times 10^{-8}\text{ cm at }20°\text{ C};$$

$$D(\mathrm{NaCl})=(2.8147\pm .0009)\times 10^{-8}\text{ cm at }20°\text{ C}.$$

The thermal expansion coefficient of these crystals, though not large, is sufficient to make corrections necessary for precise measurements. Perpendicular to the cleavage faces, this coefficient is for calcite[7] 0.0000104 and for rock salt[8] 0.0000404 per degree centigrade. If we use the value 3.02910 as the value of the grating space of calcite, and 2.81470 as that of rock salt at 20°C, their values at other temperatures are given in the following table.

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[1] H. S. Uhler, Phys. Rev. **12**, 42 (1918).

[2] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," (1915).

[3] International Atomic Weights, 1921. The estimates of the accuracy are our own, made chiefly on the basis of the data collected by F. W. Clarke, "A Recalculation of Atomic Weights" (1920).

[4] O. K. DeFoe and A. H. Compton in this issue, p. 618.

[5] R. T. Birge, Phys. Rev. **14**, 365 (1919).

[6] H. N. Beets, preceding paper.

[7] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 86 (1924).

[8] Fizeau. Cf Landolt, Bornstein, Roth "Tabellen" p. 336 (1912).

TABLE I

Grating space of calcite and rock salt at different temperatures

T	$D(\text{CaCO}_3)$	$D(\text{NaCl})$
15°C	3.02894	2.81413
16	3.02898	2.81425
17	3.02901	2.81436
18	3.02904	2.81447
19	3.02907	2.81459
20	(3.02910)	(2.81470)
21	3.02913	2.81481
22	3.02916	2.81493
23	3.02919	2.81504
24	3.02923	2.81515
25	3.02926	2.81527

It is interesting to compare these values of the grating spaces with those previously employed.

For calcite

D	Authority	Date
3.04×10^{-8}cm	W. H. Bragg[9]	1914
3.028	W. S. Gorton[10]	1916
3.0279	A. H. Compton[11]	1916
3.0307	Uhler and Cooksey[12]	1917
3.030	Millikan[13]	1917
3.0281	A. H. Compton[14]	1918
3.0283 ± .0022 } at 18° 3.02904 } at 18°	M. Siegbahn[15]	1919
3.028	Duane[16]	1920
3.02855	McKeehan[17]	1922
3.0291 ± .0010 at 20°	This determination	1925

For rock salt

D	Authority	Date
2.80×10^{-8}cm	W. L. Bragg[18]	1913
2.814	Moseley[19]	1913
2.814	E. Wagner[20]	1916
2.810	Davey[21]	1921
2.814	Siegbahn[22]	1924
2.815	Davey[23]	1924
2.8147 ± .0009 at 20°	This determination	1925

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[9] W. H. Bragg, Proc. Roy. Soc. A **89**, 468 (1914).

[10] W. S. Gorton, Phys. Rev. **7**, 209 (1916).

[11] A. H. Compton, Phys. Rev. **7**, 655 (1916).

[12] H. S. Uhler and C. D. Cooksey, Phys. Rev. **10**, 645 (1917); by comparison, assuming $D(\text{NaCl})=2.8140$ A.

[13] R. A. Millikan, Phil. Mag. **34**, 13 (1917).

[14] A. H. Compton, Phys. Rev. **11**, 431 (1918).

[15] M. Siegbahn, Phil. Mag. **37**, 601 (1919); 3.02904 obtained by comparison, assuming $D(\text{NaCl})$ at $18°=2.81400$ A.

[16] W. Duane, Bull. Nat. Res. Council No. 7 (1920).

[17] L. W. McKeehan, Science, N. S. **56**, 757 (1922); average by comparison with rock salt.

[18] W. L. Bragg, "X-Rays and Crystal Structure," (1915) p. 110.

[19] H. G. J. Moseley, Phil. Mag. **26**, 1024 (1913).

[20] E. Wagner, Ann. der Phys. **49**, 625 (1916).

[21] W. P. Davey, Science, **54**, 497 (1921).

[22] [23] See footnotes on the next page.

There has heretofore been a discrepancy between the observed and the calculated values of the ratio $D(\mathrm{CaCO_3})/D(\mathrm{NaCl})$, which has seemed larger than the probable error of the determinations.[24] It will be noticed that this ratio does not involve N, which is responsible for the greatest part of the probable error of D. Our calculated value of this ratio is $1.0762 \pm .0002$ at 18°, in which the greatest part of the uncertainty is due to the molecular weights. This is to be compared with Uhler and Cooksey's[12] value 1.07701 and Siegbahn's[15] value 1.076417 at 18°, both of which were determined by direct spectrometric methods. It will be seen that the agreement with Siegbahn's value, which is the more accurate of the two experimental determinations, is almost within the estimated probable error. There thus remains no significant discrepancy between the calculated and the observed ratios of the grating spaces of rock salt and calcite.

In view of the fact that calcite crystals are much more nearly perfect than are those of rock salt, it is natural to choose calcite for our basis of wave-length measurements. It is a fortunate, though largely fortuitous circumstance that the value which we obtain for the grating space of calcite at 18° is identical with that employed by Siegbahn, namely 3.02904 A. Thus as far as the grating space is concerned our results suggest no correction whatever to his values.

In order to get absolute wave-length measurements it is of course necessary to take into account the refraction of the x-rays in the diffracting crystal. As Ewald and others have shown, if the x-rays are of considerably higher frequency than the maximum critical frequency of the diffracting crystal, this correction can be made by merely altering slightly the grating space.[25] In this case[26]

$$\delta = ne^2\lambda^2/2\pi mc^2, \tag{4}$$

where n is the number of mobile electrons per unit volume of the crystal, e, m and c have their usual meaning, and λ is the wave-length of the incident rays. If the number of effective electrons per atom is equal to the atomic number, this becomes for calcite[27]

$$\delta = 3.67\lambda^2 \times 10^{-6}$$

if λ is expressed in angstroms. If this value is substituted in Eq. (2),

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[22] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 20 (1924).

[23] W. P. Davey, General Electric Review, **27,** 744 (1924).

[24] Cf A. H. Compton, Phys. Rev. **11,** 431 (1918); M. de Broglie, "Les Rayons X" p. 34 (1922); and especially M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 87 (1924).

[25] P. P. Ewald, Phys. Zeit. **21,** 617 (1920).

[26] A. H. Compton, Phil. Mag. **45,** 1123 (1923).

[27] A. H. Compton, l.c.[26] p. 1129.

noting that $\sin\theta = n\lambda/2D$ to a sufficient approximation, we obtain

$$n\lambda = 2D\sin\theta(1-0.0000147\ D^2/n^2). \tag{5}$$

The true wave-length may then be calculated from Eq. (1) if, for the first order of reflection from calcite, we use an effective grating space of 3.0291 (1 − 0.000135) = 3.0287 A.

For rock salt the corresponding correction factor is (1 − 0.000096). That is, to find the true wave-length we must use for the first order spectrum an effective grating space of 2.8144 A at 20°C.

As a typical case of the determination of absolute wave-length we may consider the $K\alpha_1$ line of molybdenum. Using 3.02904 A as the grating space of calcite at 18°, Siegbahn gives for this wave-length[28] 0.70759 A. Though our present work gives the same value for the true grating space, the correction due to refraction changes[29] the effective grating space for the first order spectrum to 3.02864, reducing the wave-length to 0.70749 A.

We accordingly recommend the following values as the most probable in light of this investigation:

$$D(\mathrm{CaCO_3}) = (3.0291 \pm .0010)\times 10^{-8}\ \mathrm{cm\ at\ 20^\circ\ C.}$$

$$D(\mathrm{NaCl}) = (2.8147 \pm .0009)\times 10^{-8}\ \mathrm{cm\ at\ 20^\circ\ C.}$$

$$\mathrm{Mo}\ K\alpha_1\ \text{line},\ \lambda = 0.70749 \pm .00023\ \mathrm{A.}$$

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[28] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 102 (1924).

[29] Professor Siegbahn informs us that he has applied a correction of this character to some of his most recent wave-length determinations.