JUNE 1, 1932 PHYSICAL REVIEW VOLUME 40

A Precision Comparison of Calculated and Observed Grating Constants of Crystals

By Yuching Tu
Ryerson Physical Laboratory, University of Chicago, Chicago, Ill.

(Received April 18, 1932)

A precision comparison of the calculated and observed grating constants of calcite, rocksalt, artificial KCl, and diamond crystals is made with calcite as standard. The calculated values are determined from density measurements, while the observed values are calculated from the angles of reflection for the Mo $K\alpha_1$ line obtained by means of a precision double-crystal spectrometer. The value of λ obtained from the calculated grating constant of calcite is used to determine the observed grating constants of the other crystals. The density of rocksalt and KCl is measured by immersion in Russian mineral oil whose density and change of density with temperature was found to be 0.88011 at 24°C. and 0.000064 per 0.1° respectively .The density of diamond is determined by weighing a solution of thallous formate and thallous malonate, in which the diamond just floats, in a calibrated specific gravity bottle of approximately 50 cc capacity. Two methods are used in the x-ray measurements, namely, the calcite method, de scribed by A. H. Compton and S. K. Allison and J. H. Williams, and the rocksalt method. The latter consists of measuring the peak position of the beam reflected from crystal B by swinging the ionization chamber past the beam, with two narrow slits between it and the crystal, ranging in width from 0.04 to 0.08 mm and separated by a distance of 18 cm. Calculated and observed values of the grating constants of these crystals are found to agree within experimental error, ranging from 0.004 to 0.011 percent, showing no evidence of Zwicky's "secondary structure," which he offered as a possible explanation of the discrepancy between x-ray wave-lengths obtained by the crystal method and those by the ruled grating method. Measurements on two quartz crystals showed a decided variation in the internal structure of the crystal, and indicate that quartz is unsuitable for precise wave-length measurements.

Introduction

It HAS been known that x-ray wave-lengths measured by crystals are less than those measured by ruled gratings by about 0.2 percent. Zwicky[1] offered as a possible explanation of the difference, the existence in crystals, of a "secondary structure" consisting of perfect crystal blocks, surrounded by planes whose density is larger than that of the crystal proper, thereby making the calculated grating constants smaller than those observed by means of x-rays. In other words, when calculated values of grating constants are used without taking into account this secondary structure, the wave-lengths obtained should be too small. By assuming a difference of 10 percent in the density of the secondary planes and the reflecting planes, and the existence of one secondary plane for every 30 reflecting planes, Zwicky calculated that there should be a relative correction for density of approximately 0.01, thereby giving a relative correction for grating constant of 0.003. This investigation is undertaken to compare the calculated and observed grating constants of various crystals with the purpose of discovering any difference which might explain the discrepancy between the two methods of measuring x-ray

---

[1] F. Zwicky, Proc. Nat. Acad. Sci. **16**, 211 (1930).

wave-lengths. Since the absolute value of the wave-length used must be assumed to be unknown, only relative values can be obtained from this investigation. Consequently, some crystal has to be chosen as a standard. Calcite is chosen to serve as such a standard.

General Procedure

The grating constant of calcite is calculated from its density by assuming a value for Avogadro's number. Since only relative results are sought for in this case, it is immaterial which value is chosen. Both 6.064×10^{23}, as given by Birge,[2] and 6.0594×10^{23} are used in the calculations. The value of D thus obtained is used to determine the wave-length of the Mo $K\alpha_1$ line, which is the wave-length used in this experiment, from the angle of reflection obtained from the x-ray measurements. This value of λ is then used to determine the observed grating constants of all other crystals. It should be noted here that no importance whatsoever is attached to the value of λ thus obtained as an absolute value.

Methods of Observation

A. X-ray measurements

The x-ray measurements are made by means of a precision double-crystal spectrometer of the type described by Compton.[3] Two methods are used

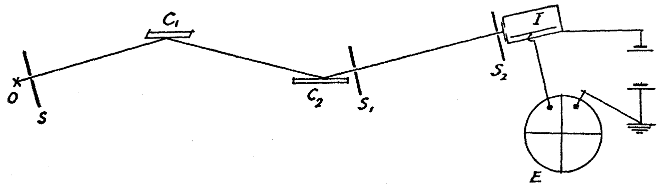

Fig. 1.

(1) the calcite method, the details of which are described by Compton, Allison and Williams,[4] (2) the rocksalt method. The calcite method is characterised by the narrow width of the rocking curve, which serves as a criterion of the accuracy of adjustment. Rocksalt, being an imperfect crystal, has a large angular range of reflection. No narrow rocking curve can be obtained from it. To obtain the desired accuracy in this case, a different method has to be used, which for convenience, is labelled the "rocksalt method." Fig. 1 is a diagrammatic sketch showing the general arrangement.

The principle of the method is based on the assumption that however imperfect the crystal may be, the peak of the beam reflected from it must make an angle with the incident beam equal to twice the angle required by Bragg's law, subject only to correction due to divergence of the incident beam and index of refraction. Naturally, a system of narrow slits is necessary in order to determine the angle accurately. By setting the crystal near the range of

---

[2] R. T. Birge, Phy. Rev. Supplement **1**, 1 (1929).

[3] A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931).

[4] S. K. Allison and J. H. Williams, Phy. Rev. **35**, 1476 (1930).

maximum reflection, and observing the peak of the beam with an ionization chamber for both the parallel and anti-parallel positions, 4θ is obtained.

O is the x-ray source furnished by a Coolidge water-cooled Mo tube run at 50 k.v. peak voltage and 25 m.a. C_1 is a calcite crystal (referred to later as crystal A); C_2 is rock-salt crystal (referred to later as crystal B). Both crystals are mounted on holders which permit micrometer adjustments in the horizontal plane in two directions, one perpendicular to the crystal face, and one parallel to it. The former adjustment can be made to a fraction of 0.01 mm. The holders are mounted on tables with levelling screws to adjust the vertical tilt of the crystals. S_1 and S_2 are two narrow slits, generally from 0.04 mm to 0.08 mm width, depending upon the intensity of the beam. I is an ionization chamber of a type described by Compton, filled with krypton gas at atmospheric pressure. E is a Compton electrometer set at a sensitivity of 8000 scale divisions per volt.

Adjustments

1. To set crystal A parallel to the axis of rotation of crystal B. A calcite crystal is mounted on the crystal B holder and set parallel to its axis of rotation and over the center of rotation by a method described below. The vertical tilt of crystal A is adjusted until the smallest width of the rocking curve of crystal B is obtained in the parallel position.

2. To set crystal B parallel to the axis of rotation and directly over the center of rotation. An optical parallel plate glass is set over the center of the crystal table. A telescope with a Gauss eyepiece is used to observe the image of the cross-hairs reflected from the glass. Both the crystal table and the telescope are levelled until the image of the horizontal cross-hair coincides with the hair itself as seen in the eyepiece both before and after the crystal table is turned through 180°. This makes the axis of the telescope perpendicular to the axis of rotation of the crystal table. As the rocksalt cleavage face is not perfect enough to obtain a clear image of the cross-hair, the optical plane glass is set flat against the crystal face by tying it to the crystal holder with a rubber band. The crystal table is then levelled to make the two images coincide. To set the crystal face over the center of rotation, a sharp point is placed over the table and adjusted until it does not change its position when the table is rotated around, as seen in a microscope. The crystal face is then brought close to the point until the point and its image in the crystal just come into contact as seen in the microscope. An accuracy of 0.01 mm can easily be obtained.

3. To set the slits S_1 and S_2 parallel to the axis of rotation of crystal B. An optical plane glass is set parallel to the axis as before. A thin plane mirror is set between the jaws of the slit S_1. S_1 is near enough to the crystal table so that the reflections of a scale in the glass and the mirror can be viewed side by side in the same field of a telescope placed about 2 meter distant from either. The slit is then rotated until the same reading is obtained as from the glass. The error of adjustment is not more than 10 seconds of arc. By using an

auxiliary mirror which is long enough to stretch over the distance between the two slits and the same method, S_2 is set parallel to S_1.

4. To make the beam reflected from crystal A pass through the axis of rotation of crystal B. An approximate adjustment is made by moving crystal A in a horizontal plane until the same deflection of the electrometer is observed before and after crystal B is turned around 180°, with one of the slits, S_1, opened wider than S_2. To make the final adjustment, the slit at the x-ray tube is made very narrow, 0.02 mm. An optical plane glass is tied to crystal B, and separated from the latter at the top and bottom by a strip of aluminum 0.02 mm thick. This makes a slit at the center of the table $16\times 20\times 0.02$ mm. The slit S_2 is also made 0.02 mm wide, and the x-ray beam made to pass through these two slits and give the same deflection before and after the crystal is turned through 180°. This test also checks whether or not crystal B is set accurately over the center. S_1, also made 0.02 mm wide, is then shifted laterally until the same deflection is observed as when it is opened wide. This then makes the line joining the slits S_1 and S_2, and the x-ray beam pass through the axis of rotation of crystal B. Provided all the adjustments are correct, the curves taken by swinging the ionization chamber pass the beam ought to be symmetrical. A series of curves are taken to test the effect of alignment on the shape of the curves. (Figs. 2 and 3)

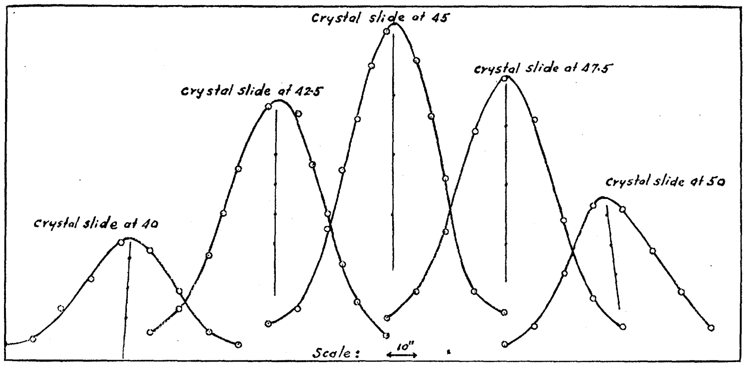

Fig. 2. Effect of changing position of crystal A.

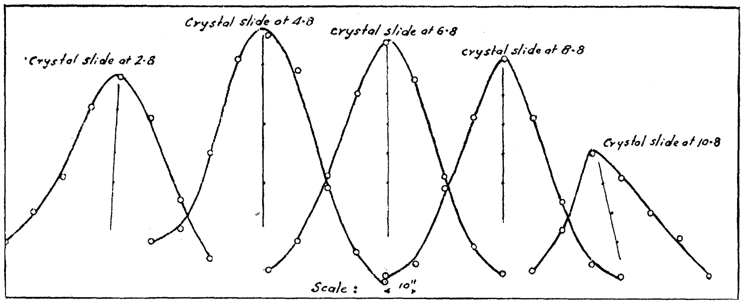

Fig. 3. Effect of changing position of crystal B.

A difference of 1 in the crystal slide reading means a shift of the crystal of 0.01 mm parallel to itself. From the curves it can be easily seen that a displacement of either one of the crystals of 0.1 mm or 0.08 mm produces a decided difference in the symmetry of the curves. As the beam sweeps across the face of the crystal, the curve first leans to one side, becomes symmetrical, and then leans to the other side. The curves with good symmetry invariably give much larger peak intensities. The width at half-maximum of these curves is about 40″, which is nothing but the angle subtended by the two slits, the slits being 0.04 mm wide, and 18 cm apart.

From these adjustments and tests, it is concluded that the criterion of accuracy of adjustment for the "rocksalt method" is the symmetry of the curve. This method has been used for rocksalt, artificial KCl, and quartz crystals. However, wherever it is possible, the calcite method is used as a check.

With diamond crystal, an additional factor needs to be considered. Diamond is known to be a perfect crystal, but the faces are polished without regard to their parallelism to the natural reflecting planes. Rotation photographs are taken to ascertain the planes nearest to the polished faces. In both of the diamonds, the 100 plane is found. But in the one case, the angle of tilt is about 2°, while in the other it is about 8°. To eliminate any error which may arise due to this tilt, measurements are taken with various orientations of the crystal with respect to the x-ray beam. Since the diamonds are cut square, the orientations are changed either by 90° or 180°. For both diamonds, the calcite method is used.

B. Density measurements

All density measurements are made on the same crystal or crystal block as the x-ray measurements. The density of calcite and quartz is determined by the immersion method, with distilled water as the liquid. A wire loop is used to hold the crystal in the liquid. The weight of the loop in the liquid is obtained by removing the crystal from the loop, the crystal still remaining in the liquid. The difference between the two weighings gives directly the weight of the crystal in the liquid without any corrections.

The density of rocksalt and KCl is determined by immersion in Russian mineral oil. It is not only necessary to determine the density of the oil, but also its change with temperature. To determine the latter, two quartz crystals, a rocksalt and a KCl crystal are used and the temperature noted at each weighing. The weighings of the two quartz crystals, after reduction to the same temperature are used to calculate the density of the oil at that particular temperature. In calculating the change of density with temperature, the thermal expansion of the crystals has been taken into account. Table I gives the results in a condensed form. The temperature difference observed ranges from 0.2 to 0.6 degree.

For the density of diamond, resort has to be made to an entirely different method, as the crystals are far too small to use the immersion method to obtain any reasonable degree of accuracy. A solution[6] of thallous formate and thallous malonate can be made to have a density of 4 or more, so that the diamond can float in it. At first, it was attempted to determine the density of the liquid by the ordinary method of immersion, after it has been made to the desired concentration. But it was found that successive weighings in the same solution did not agree very well with each other. It was either due to the change of density with evaporation, although the container was covered, change of density with temperature, or due to the existence of a density gradient in the liquid. The first two factors can be eliminated by weighing the liquid in a specific gravity bottle with a vacuum jacket to maintain constant temperature. Due to the probable existence of a density gradient in the liquid, there is no clear demarcation between the solution in which the diamond floats and that in which it sinks. The only way to overcome this difficulty is to narrow down the range of uncertainty by gradually diluting a solution in which the diamond unquestionably floats and making more concentrated a solution in which it undoubtedly sinks. Near and within the range there will be times when the diamond will float somewhere in the middle of the liquid. The range thus found represents 0.036 percent of the total weight of the liquid for the smaller diamond, and 0.019 percent for the larger one.

TABLE I. *Change of density of Russian mineral oil with temperature. Densities of crystals used*

Crystal	cub. exp.[5] coef. $\times 10^{-4}$	approx. vol. cc	decrease in wt. per 0.1° due to expansion of crystal	obs. increase per $0.1° \times 10^{-4}$ gm	true change $\times 10^{-4}$ gm	change in density per 0.1°
quartz$_1$	0.384	57.32	1.93	36.6	38.5	6.7×10^{-5}
quartz$_2$	0.384	41.90	1.42	20.8	22.2	5.3×10^{-5}
rocksalt	1.212	5.68	.6	3.48	4.08	7.2×10^{-5}
KCl	1.094	14.24	1.37	7.44	8.81	6.2×10^{-5}

The average change of density of oil per 0.1° $=6.4\times 10^{-5}\pm 0.5\times 10^{-5}$. From this value of change of density, the first quartz crystal gives 0.88010 for the density at 24°C and the second gives 0.88012 giving an average value of 0.88011 at 24°C.

CORRECTIONS

1. Vertical divergence

In the x-ray measurements, correction must be applied to the angle of reflection due to the vertical divergence of the incident beam according to the formula.[3]

$$\delta\theta = \tfrac{1}{2}\alpha^2 \tan\theta$$

where α is the angle of vertical divergence, and θ the observed angle of reflection. By integrating over the two slits

$$\delta\theta = \frac{1}{24}\,\frac{a^2+b^2}{L^2}\tan\theta$$

where a and b are the slit heights and L the distance between them.

---

[5] Smithsonian Tables, p. 220, 1923.

[6] R. G. O'Meara and J. B. Clemmer, Chem. Abstracts **23**, 1589 (1929).

For the rocksalt method, the same correction should be applied. In order to find out whether the same formula applies to this case or not, the angle of reflection for calcite has been measured by both methods, the rocksalt method giving a value larger by 1.1″. The correction as calculated from the formula, from the slit heights used, comes out to be 1.3″, showing the formula can be applied to the rocksalt method. However, in order to increase the intensity in the case of rocksalt, KCl and quartz, higher slits are used (both a and b are 1.7 cm) and L 58 cm), giving a larger correction.

2. Index of refraction

To correct for the index of refraction the ordinary formula is used, namely,

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

where δ is calculated from the equation

$$\delta = ne^2/2\pi mv^2.$$

3. Calibration of the circle

The crystal circle has been calibrated.[3] It has been found that the circle can be relied on to 1″ of arc without correction. It has also been found that the largest errors in the calibration came in the microscope readings of the circle graduations. The ionization chamber circle has not been calibrated, but can be assumed to have the same degree of accuracy. Corrections for the ionization chamber observations are made by assuming the same curve for calibration.

4. Temperature effect on angle measurements

The correction for angle measurements due to temperature is calculated from the equation $d\theta = -\alpha(t-18) \tan \theta$, where α is the expansion coefficient of the crystal. This gives the corrections per degree of temperature shown in Table. II.

TABLE II. *Angle corrections per degree temperature.*

Crystal	Linear expansion coef.	Angle correction per degree of temp.
Calcite	$1.04.10^{-5}$	0.25″
Rocksalt	$4.04.10^{-5}$	1.07″
KCl	$3.65.10^{-5}$	0.86″
Quartz	$1.28.10^{-5}$	0.22″ for the A face 0.28″ for the 101 face
Diamond*	$0.118.10^{-5}$	0.11″ for the 400 face

* Int. Critical Tables: Vol. III, p. 21.

RESULTS

A. Angle measurements

All the angles given in Tables III–IX are corrected for circle calibration and reduced to 18°C. The results for calcite in the first order for both cleavage and polished faces are given in Tables III and IV.

TABLE III. *Angle measurements. Calcite—natural cleavage face, first order.*

	Slit height, 6.5 mm		Slit height,† 3 mm		Slit height,† 0.8 mm	
	Angle	Width at ½ max.	Angle	Width at ½ max.	Angle	Width at ½ max.
	6°-42′-35.6″	4.5″	6°-42′-36.4″	5.7″	6°-42′-35.2″	6.6″
	35.6″	4.8″	35.0″	5.4″	35.1″	6.8″
	36.9″	4.8″	35.8″	5.8″	35.6″	6.8″
	36.2″	4.1″	35.2″	5.5″	35.2″	6.4″
	35.5″	4.7″				
	36.2″	4.3″				
	36.2″	4.9″				
	36.5″	4.6″				
	36.2″	4.9″				
Aver.	6°-42′-36.1″		6°-42′-35.6″		6°-42′-35.3″	
Corrected for vertical divergence	6°-42′-35.6″		6°-42′-35.5″		6°-42′-35.3″	
Resulting average 6°-42′-35.5″±0.1″						

† These were taken after a complete new alignment.

TABLE IV. *Angle measurements. Calcite—polished face, first order.*

	Slit height, 3 mm		Slit height 0.8 mm	
	Angle	Width at ½ max.	Angle	Width at ½ max.
	6°-42′-35.8″	12.0″	6°-42′-35.8″	12.6″
	36.6″	11.8″	35.9″	11.0″
	36.7″	11.4″	36.0″	12.0″
	36.5″	11.5″	35.7″	11.6″
	35.3″	11.6″	36.2″	11.2″
	35.9″	12.7″		
	36.0″	11.6″		
	35.9″	11.8″		
	35.5″	11.9″		
Aver.	6°-42′-36.2″		6°-42′-35.9″	

When corrected for divergence these give an average of 6°-42′-36.0″±0.1″, which is 0.5″ larger than that found for the cleavage face. The difference is probably due to the fact the polished face is not quite parallel to the original cleavage face.

Table V gives the results for calcite of the angle β between the axes. A piece is cleft from the same block as the crystals used above. Two good adjacent faces are used for this measurement. The line of intersection between the faces is set parallel and over the axis of rotation by the method previously described. The accuracy of the adjustment is borne out by the fact that the

TABLE V. *Angle measurements. Calcite—angle β between axes.*

Width of rocking curve Face 1	Face 2	Slit height	Angle α	Corrected angle
6.4″	6.2″	0.8 mm	105°-3′-23.9″	105°-3′-23.6″
7.4″	7.2″	2.0 mm	105°-3′-24.9″	105°-3′-23.4
6.6″	6.7″	0.8 mm	105°-3′-24.5″	105°-3′-24.2″
			Aver.	105°-3′-23.7±0.3″

widths of the rocking curves in the (1, −1) position are practically the same for both faces. The angle the crystal is rotated through between the two (1, −1) peaks gives the horizontal projection of the dihedral angle between the faces, from which the angle β can be calculated. Three different settings give the following values shown in Table V.

The angle β can be calculated from the equation

$$\cos \tfrac{1}{2}\beta = \frac{1}{2 \sin \frac{1}{2}\alpha},$$

giving

$$\beta = 101°\text{–}54' - 0.4'' \pm 0.3''$$

The unit volume of the crystal is then found from

$$\phi(\beta) = \frac{(1 + \cos \beta)^2}{(1 + 2 \cos \beta) \sin \beta}\,.$$

$$= 1.09592 \text{ at } 23°.5\text{C or } 1.09602 \text{ at } 18°\text{C}^7$$

Measurements by the optical method with a telescope with a Gauss eye-piece give 105°–3′–11.9″ as an average of five readings, which is some 12″ smaller than that obtained from the x-ray measurements. This incidentally

TABLE VI. *Angle measurements. Rocksalt—cleavage face, first order.*

	1st setting	2nd setting	Polished face
	7°–13′–36.0″	7°–13′–35.2″	7°–13′–37.0″
	7°–13′–36.4″	7°–13′–34.3″	7°–13′–37.4″
	7°–13′–35.5″	7°–13′–35.2″	7°–13′–38.1″
	7°–13′–36.7″	7°–13′–34.9″	7°–13′–35.9″
	7°–13′–36.7″	7°–13′–35.4″	7°–13′–36.1″
	7°–13′–36.7″	7°–13′–35.4″	7°–13′–36.4″
	7°–13′–36.1″	7°–13′–36.0″	7°–13′–38.6″
	7°–13′–35.9″	7°–13′–36.7″	
Aver.	7°–13′–36.3″	7°–13′–35.4″	7°–13′–37.1″

TABLE VII. *Angular measurements. KCl—natural cleavage face, first order.*

	1st setting	2nd setting	3rd setting
	6°–28′–28.8″	6°–28′–28.7″	6°–28′–27.9″
	6°–28′–28.8″	6°–28′–31.1″	6°–28′–28.8″
	6°–28′–29.2″	6°–28′–29.4″	6°–28′–28.4″
	6°–28′–28.7″	6°–28′–303.″	6°–28′–28.3″
			6°–28′–29.1″
			6°–28′–29.8″
			6°–28′–31.1″
			6°–28′–28.5″
Aver.	6°–28′–28.9″	6°–28′–29.9″	6°–28′–29.0″

---

[7] H. N. Beets, Phy. Rev. **25,** 621 (1925). $\phi(\beta)$ increases by 0.000018 per degree of decrease in temp.

gives an idea of the accuracy attainable in adjusting the second crystal parallel to its axis of rotation.

The results for rock salt are given in Table VI. The average of the two sets there given, after correcting for vertical divergence, gives 7°–13′–34.0″ ±0.3″. The measurements on KCl are presented in Table VII.

The average of three settings is 6°–28′–29.3″ and when corrected for divergence this becomes 6°–28′–27.6±0.3″. Measurements were made on two diamond crystals. They are summarized in Tables VIII and IX.

TABLE VIII. *Angular measurements. 0.89 karat diamond—polished, 400 plane.*

	Position 1	Width at ½ max.	Position 2 (Position 1 turned 180°)	Width at ½ max.
	23°–26′–5.6″	50″	23°–26′–6.3″	45″
	23°–26′–5.9″	50″	23°–26′–6.9″	45″
	23°–26′–5.5″	48″	23°–26′–7.0″	43″
	23°–26′–5.0″	48″	23°–26′–7.7″	47″
Aver.	23°–26′–5.5″		23°–26′–7.0″	
		Average:	23°–26′–6.3″	
		Corrected for div.:	23°–26′–3.6″±0.5″	

TABLE IX. *Angular measurements. 1.78 karat diamond—polished, 400 plane.*

	Position 1	Position 2 (Position 1 turned through 180°)	Position 3 (Position 1 turned through 90°)	Position 4 (Position 3 turned through 180°)
	23°–26′–5.7″	23°–26′–11.8″	23°–26′– 8.6″	23°–26′–6.3″
	23°–26′–6.5″	23°–26′–12.3″	23°–26′–10.9″	23°–26′–6.5″
	23°–26′–6.4″	23°–26′–11.4″	23°–26′– 9.9″	23°–26′–6.8″
	23°–26′–5.8″	23°–26′–12.9″	23°–26′–10.3″	23°–26′–6.0″
	23°–26′–6.8″	23°–26′–11.8″	23°–26′–10.2″	23°–26′–6.2″
	23°–26′–6.7″	23°–26′–11.1″	23°–26′–11.5″	
	23°–26′–6.0″			
	23°–26′–6.6″			
Aver.	23°–26′–6.3″	23°–26′–11.9″	23°–26′–10.2″	23°–26′–6.4″
Average:	23°–26′–9.1″		23°–26′–8.3″	
	Grand average:	23°–26′–8.7″±0.4″		
	Corrected for div.:	23°–26′–6.0″±0.4″		

B. Density measurements

The density measurements are summarized in Tables X, XI and XII.

TABLE X. *Density measurements.*

Calcite			Rocksalt		
Density	Temp. deg. C	Density at 18°C	Density	Temp. deg. C	Density at 18°C
2.70976	27.1	2.71009	2.16282	24.4	2.16450
2.70970	26.6	2.71002	2.16234	24.5	2.16404
2.70975	26.5	2.71007	2.16219	24.7	2.16395
2.70973	27.5	2.71009	2.16231	25.1	2.16417
2.70960	22.9	2.70990	2.16239	25.0	2.16422
	Average	2.71003 ±.00005			2.16418 ±.00014

TABLE XI. *Density measurements. KCl.*

Density	Temp.	Density at 18°C
1.98797	24.5	1.98933
1.98743	24.8	1.98885
1.98792	24.8	1.98934
1.98798	24.8	1.98940
1.98792	24.9	1.98936
1.98786	25.0	1.98932
1.98757	25.1	1.98905
1.98797	25.3	1.98949
1.98796	25.4	1.98951
1.98781	25.5	1.98938
		Average: 1.98930 ± 0.00014

TABLE XII. *Density measurements. Diamond.*

	0.89 karat diamond			1.78 karat diamond		
	Weight of bottle and liquid			Weight of bottle and liquid		
	Just floating	Just sinking	Floating in middle	Just floating	Just sinking	Floating in middle
	235.629	235.560	235.611	235.623	235.586	235.595
	235.621	235.575	235.611	235.623	235.591	235.603
	235.630	235.569	235.618	235.625	235.595	235.608
	235.627	235.557				235.619
		235.555				235.614
Aver.	235.6268	235.5632	235.6133	235.6243	235.5907	235.6064
Aver.:	235.5950		235.6133	235.6075		235.6064
Aver.:	235.6042			235.6070		
Calculated density at 18°C	3.5141 ± 0.0001			3.5142 ± 0.0001		

C. Calculation of grating constants

From the values of density and angles obtained, the values of calculated and observed grating constants are calculated and set forth in Tables XIII. The observed values are given in Table XIV.

TABLE XIII. *Calculated grating constants.*

Crystal	No. Mol. per unit cell	M	Unit vol.	Density at 18°C	Grating constant $N=6.0594 \times 10^{23}$	Grating constant $N=6.064 \times 10^{23}$
Calcite	½	100.075[2] ±0.005	1.09602 ±0.00001	2.71003 ±0.00005	3.02940 ±0.00005	3.03863 ±0.00005
Rocksalt	4	58.454*	1	2.1642 ±0.0001	2.81418 ±0.00005	2.81347 ±0.00005
KCl	4	74.557	1	1.9893 ±0.0001	3.13889 ±0.00005	3.13810 ±0.00005
Diamond (0.89 k)	8	12.003[2] ±0.001	1	3.5141 ±0.0001	3.55942 ±0.00009	3.55852 ±0.00009
Diamond (1.78 k)		12.003 ±0.001	1	3.5142 ±0.0001	3.55938 ±0.00009	3.55848 ±0.00009

* Mol. wt. of NaCl.

Table XIV. *Observed grating constants.*

Crystal	Face	Angle	$1-\mu\times10^{-6}$	Grating constant $N=6.0594$ $\times10^{23}$	 $N=6.064$ $\times10^{23}$
Calcite	Cleavage	6–42′–35.5″ ±0.1″	1.85		
Rocksalt	100	7–13′–34.0″ ±0.3″	1.41	2.81387 ±0.00005	2.81316 ±0.00005
KCl	100	6–28′–27.6″ ±0.3″	1.31	3.13900 ±0.00005	3.13822 ±0.00005
Diamond (0.89 k)	400	23–26′– 3.6″ ±0.5″	2.39	3.55966 ±0.00005	3.55875 ±0.00005
Diamond (1.78 k)	400	23–26′– 6.0″ ±0.5″	2.39	3.55956 ±0.00005	3.55866 ±0.00005

The differences between the calculated and observed grating constants are given in Table XV.

Table XV. *Difference between the calculated and observed grating constants.*

Crystal	Calculated value	Observed value	$\dfrac{D_{\text{cal.}}-D_{\text{obs.}}}{D_{\text{cal.}}}$
Calcite	3.02940		
Rocksalt	2.81418	2.81387	0.011%
KCl	3.13889	3.13990	−0.004%
Diamond (0.89 k)	3.55942	3.55966	−0.007%
Diamond (1.78 k)	3.55938	3.55956	−0.005%

For the sake of comparison the results of some of the other investigators are included in Table XVI. Since no accurate results are recorded for the

Table XVI. *Comparison with results of others.*

Angle cleavage face	Author	Density	Author	Unit volume	Author
6°–42′–34.3″	Leide[8]				
6°–42′–35.4″	Larsson[9]				
6°–42′–33.3″	Allison and Armstrong[10]	2.7102	Defoe and Compton[13]	1.09634	Beets[14]
6°–42′–36.0″	Compton[11]				
6°–42′–35.3″ to 35.6″	Bearden[12]	2.71026	Bearden[12]	1.09598	Bearden[12]
6°–42′–35.5″	Present	2.71003*	Present	1.09602	Present

Note: All values given above are reduced to 18°C.

* The author also made a density determination on a calcite crystal which is polished all around, giving a value of 2.71010.

---

[8] A. Leide, Comptes Rendus **180,** 1203 (1925).

[9] A. Larsson, Phil. Mag. **3,** 1136 (1927).

[10] S. K. Allison and A. H. Armstrong, Phy. Rev. **26,** 701 (1925).

[11] A. H. Compton, corrected by J. H. Williams, Letter to the Editor, Phy. Rev. May 15, 1932.

[12] J. A. Bearden, Phy. Rev. **38,** 1389 (1931).

[13] O. K. Defoe and A. H. Compton, Phy. Rev. **25,** 618 (1925).

[14] H. N. Beets, Phy. Rev. **25,** 621 (1925).

crystals used in this investigation with the exception of calcite, only those for calcite are listed below.

For rocksalt, using Siegbahn's[15] precise comparisons between the grating constants of rocksalt and calcite, and the value of D for calcite, adopted as a standard here, it is found that the D for rocksalt would be 2.81421 as compared with 2.81387 obtained above.

Defoe and Compton's measurement of the density of rocksalt gave 2.1637 ± 0.0004 as compared with 2.1642 obtained by the author.

Data for Quartz Crystals

Angle measurements on quartz crystals are presented in Table XVII, XVIII and XIX.

Table XVII. *Angle measurements. Quartz (1)–(100) face.*

	Face 1 (polished)		Face 2		Face 3
	Position 1	Position 2	Natural	Polished	natural
	4°–46′–55.2″	4°–46′–54.0″	4°–46′–37.9″	4°–46′–36.5″	4°–46′–37.2″
	4°–46′–54.8″	4°–46′–53.2″	4°–46′–37.9″	4°–46′–36.9″	4°–46′–37.4″
	4°–46′–55.4″	4°–46′–54.1″	4°–46′–37.3″	4°–46′–36.7″	4°–46′–37.5″
	4°–46′–52.6″	4°–46′–53.1″	4°–46′–38.4″	4°–46′–36.6″	4°–46′–37.3″
	4°–46′–54.6″				
	4°–46′–53.9″				
	4°–46′–54.7″				
Av.	4°–46′–54.3″	4°–46′–53.6″	4°–46′–37.9″	4°–46′–36.6″	4°–46′–37.4″
Corr.	4°–46′–53.1″	4°–46′–52.4″	4°–46′–36.7″	4°–46′–35.4″	4°–46′–36.2″
	±0.6″	±0.4″	±0.3″	±0.2″	±0.1″

Table XVIII. *Angle measurements. Quartz (1)–(101) face.*

	Face 3	Face 3	Face 4	Face 5
	Rocksalt method	Calcite method	Polished	natural
	natural			
	6°–5′–26.5″	6°–5′–25.9	6°–5′–27.2″	6°–5′–31.7″
	6°–5′–27.8″	6°–5′–25.1″	6°–5′–28.1″	6°–5′–31.5″
	6°–5′–28.0″	6°–5′–26.2″	6°–5′–27.9″	
	6°–5′–28.5″		6°–5′–27.3″	
Av.	6°–5′–27.7″	6°–5′–25.7″	6°–5′–27.6″	6°–5′–31.6″
Corr.	6°–5′–26.1″	6°–5′–25.4″	6°–5′–26.0″	6°–5′–30.0″
	±0.7″	±0.4″	±0.3″	

Discussion of Results

Bearden,[16] using the value he obtained for the Cu $K\alpha$ line from a ruled grating and the value of sin θ obtained by Siegbahn and Dolejsek from crystal measurements, and Larsson's value for the correction for index of refraction, obtained 3.0359 ± 0.0003 for the grating constant of calcite. This value is 0.217 percent larger than the value obtained here, using $6.0594.10^{23}$ for Avogadro's number, and 0.243 percent larger if $6.064.10^{23}$ is used. From the results of this experiment, it can be seen that the calculated and observed grating

---

[15] M. Siegbahn, Phil. Mag. **37**, 601 (1919).

[16] J. A. Bearden: Phy. Rev. **37**, 1210 (1931).

constants agree within experimental error for calcite, KCl and diamond. The probable errors are due mainly to the probable errors in molecular weight. The results for rocksalt are not as good, the significant fact being that the deviation is in the opposite direction. As far as the four crystals used in this experiment are concerned, there is found no definite proof for the existence of the mosaic effect suggested by Zwicky, or if it does exist, it can not affect the x-ray wave-length measurements by more than 0.01 percent . It can be concluded, therefore, that the crystal method of measuring x-ray wave-lengths can be relied on to within 0.01 percent when a perfect crystal is used, provided, of course, Avogadro's number is known to the same degree of accuracy.

TABLE XIX. *Angle.measurements. Quartz* (2).

	Face 1 Natural 100 face	Face 2 Natural 101 face		Face 3 Polished 100	Face 4 101 Polished
		Rocksalt method	Calcite method		
	4°–46′–31.9″	6°–5′–19.4″	6°–5′–16.9″	4°–46′–48.5″	6°–5′–26.8″
	4°–46′–32.6″	6°–5′–18.7″	6°–5′–17.0″	4°–46′–48.2″	6°–5′–26.0″
	4°–46′–31.8″	6°–5′–19.9″	6°–5′–18.1″	4°–46′–48.2″	6°–5′–25.4″
	4°–46′–30.7″	6°–5′–19.7″	6°–5′–17.8″	4°–46′–47.3″	6°–5′–25.4″
	4°–46′–31.1″		6°–5′–18.2″	4°–46′–47.9″	
			6°–5′–17.6″		
Av.	4°–46′–31.9″	6°–5′–19.4″	6°–5′–17.6″	4°–46′–48.0″	6°–5′–25.9″
Corr.	4°–46′–30.3″	6°–5′–17.8″	6°–5′–17.3″	4°–46′–46.4″	6°–5′–24.3″
	±0.5″	±0.4″	±0.4″	±0.3″	±0.4″

The density measurements are as follows:
Quartz (1) 2.64848 at 18°C ±0.00002. Quartz (2) 2.64864 at 18°C ±0.00002.

As to the data on quartz crystals, it may be said at the outset that the crystals are not as good as one would desire from the appearance of the faces. It can be easily seen from the angle measurements that quite different values of the grating constant will be obtained, depending on which set of planes is used. The differences are far beyond any experimental error, in the light of measurements on the other crystals. The differences can not be very well ascribed to surface conditions of the faces, because measurements on the same face, both natural and polished, gave practically the same value. They are certainly not due to the method used, because both the calcite and rocksalt method, when applied to the same face, gave practically the same value, which incidentally shows the validity of the rocksalt method. The differences, therefore, must be due to some variation in the structure of the crystal. However, in order to ascertain this variation definitely, a large number of observations must be made on different faces of the same crystal, and also on different crystals. It can be concluded, however, that quartz crystals are not suitable for precise wave-length measurements.

In conclusion, the writer wishes to extend his deep gratitude to Professor A. H. Compton who suggested this problem, for his valuable help and advice throughout the investigation, and to Professors W. H. Zachariasen and S. K. Allison for their helpful suggestions. Finally, I am indebted to Mr. J. Milhening of Chicago for loaning the diamonds used in this experiment.