TESTS OF THE VALIDITY OF THE X-RAY CRYSTAL

METHOD FOR DETERMINING "e"

Thesis by

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Abstract

To establish the validity of the x-ray crystal method for determining "e", the density of microscopic powdered calcite and the x-ray diffraction angles for several sets of planes of a sample of the same powdered calcite were measured.

The density of powdered calcite was determined pycnometrically to be

$$\rho = 2.71022 \pm 0.00035 \text{ gms/cc}$$

in agreement with macroscopic calcite.

X-ray diffraction rings of the Ni $K\alpha_1$ and $K\alpha_2$ lines for planes $(3\bar{3}0)$, (677), (233) and (163) (crystallographic system of axes) were observed using a Seeman-Bohlin powder camera. The observed rings all occur at diffraction angles near $90°$ thus affording extremely high precision in the lattice constant determinations. The parameters found for powdered calcite from these data are

$$C = 12.8197 \pm 0.0016 \text{ Å (Siegbahn Scale)}$$
$$\text{and} \quad \beta = 101 \quad 54' \ 18'' \pm 48''.$$

The grating space of the cleavage planes calculated from these data is

$$d_{100} = 3.0282 \text{ Å (Siegbahn Scale of wavelengths)}$$

in agreement with d_{100} for macroscopic calcite within the experimental

error of 0.05 percent.

From the known grating wavelength of Cu Kα_1 and the experimental data for powdered calcite the value

$$e = 4.799 \pm 0.007 \times 10^{-10} \text{ e.s.u.}$$

was obtained.

This measurement constitutes the first high precision lattice determination on calcite ever made by the powder method. It is free from the objection frequently raised in the case of determinations on large calcite crystals that the density determination may not be representative of the thin layer at the surface of a crystal involved in x-ray reflection.

Introduction

The problem of establishing order in the value of the fundamental constant "e" is of great importance and has formed the basis for many researches. The various experiments relating to this question and the method of weighing the experimental results on the Bond Diagram are well known. The particular phase of this general problem treated in this research deals with the validity of x-ray crystal methods in determining "e".

X-ray wavelengths were originally measured by means of crystalline diffraction occurring according to the well known Bragg equation with Siegbahn's slight correction for the deviation of refractive index from unity

$$n \lambda = 2 d \sin \Theta \left(1 - \frac{\delta}{\sin^2 \Theta}\right)$$

The experimental procedure amounts to determining the glancing angle Θ in an order n for diffraction from a set of atomic planes of spacing d. The wavelength λ thus diffracted is expressible on a scale having the same unit as the scale for the grating space d.

The relation of the electron charge e to the measurement of x-ray wavelengths enters through the grating constant d in the Bragg equation. It is easily shown (1) that the grating space for the cleavage planes in calcite is given by

$$d = \sqrt[3]{\frac{M}{2 N \rho \Phi(\beta)}}$$

where M is the molecular weight of calcite, N the Avogadro number, ρ the density of calcite, and $\Phi(\beta)$ the volume factor given by

$$\Phi(\beta) = \frac{(1 + \cos\beta)^2}{(1 + 2\cos\beta)\sin\beta}$$

where β is the characteristic angle of the calcite cleavage rhombohedron. If Q is the value of the Faraday in electrostatic units of charge per gram equivalent, then

$$N = \frac{Q}{e}$$

and

$$d = \sqrt[3]{\frac{Me}{2\,Q\,\rho\,\Phi(\beta)}} \quad .$$

The Bragg equation for diffraction from cleavage planes can then be written as

$$(1) \qquad n\lambda = 2\sqrt[3]{\frac{Me}{2\,Q\,\rho\,\Phi(\beta)}}\left(1 - \frac{\delta}{\sin^2\Theta}\right)\sin\Theta$$

where the term $\dfrac{\delta}{\sin^2\Theta}$ is the correction for the index of refraction μ of calcite which differs from unity by an amount δ.

Wavelengths of x-rays may also be measured with considerable precision by use of ruled gratings used at grazing incidence. The wavelengths thus measured are directly expressible in centimeters. The theory and possible errors of ruled gratings used under x-ray conditions have been thoroughly investigated.[1] The results of

grating measurements are believed to be thoroughly reliable. As a result, the absolute wavelengths thus determined have been used in conjunction with equation (1) above to determine values of the electron charge e. The values thus obtained are consistently higher than Millikan's oil drop value by approximately 0.6 of one per cent.

There are thus two scales of x-ray wavelength. (I) The scale established by Siegbahn by the method described above in the last paragraph, but one on the basis of a value of e which must now be considered as more or less arbitrary. (II) The absolute scale of wavelengths established by grating measurements directly which is probably correct. Measurements of diffraction angles of characteristic x-ray lines can thus be used for the direct determination in absolute units of the crystal grating constants. From these values of d and directly measured values of the density ρ of the crystal it is thus possible to determine e. This is what we mean by the x-ray crystal method of determining e.

The existence of such a discrepancy has led to many investigations into the source of the trouble. The accepted values[2] of the molecular weight M and the Faraday Q are probably beyond suspicion. Bearden[3] has recently made a careful study of the density ρ and the characteristic angle β for macroscopic* calcite obtained from a wide variety of sources. His findings are in accord with those of other

* We use the term "macroscopic calcite" to describe pieces of dimensions large in comparison to the thickness of the surface layer which reflects x-rays as limited by the well known effect of "extinction".

workers.

One might be led to conclude that the work of Bearden and others mentioned above establishes the validity of x-ray crystal methods in determining "e" were it not for a logical hiatus which exists in the reasoning. The existence of this gap is made clearer in what follows.

The angle of diffraction Θ is observed by Bragg reflection at a cleavage surface. In this process the x-rays enter and leave the same face of the calcite crystal penetrating only a distance equal to the extinction layer. The half depth of penetration is only of the order of 4×10^{-4} cm even in a third order reflection. The effective area illuminated on the face of the crystal is at most one square centimeter. This means that a volume of only 4×10^{-4} cc of the entire crystal is being used to determine Θ. As mentioned above, the density ρ of calcite is based on macroscopic pieces at least 10 cc in volume. It is entirely conceivable that stresses existing within the crystal might produce an "effective" grating constant near the surface different from that calculated from macroscopic density measurements. The very fact that a crystal is cleaved leads one to doubt the wisdom of tacitly assuming without proof that the surface planes are truly representative of the entire macroscopic crystal.

In order to determine whether or not the internal planes of calcite give the same angles of diffraction as the external planes Brown[4] using a photographic spectrometer measured the diffraction angles of the Mo $K \alpha_1$ and $K \alpha_2$ lines diffracted from the planes (100) and (1$\bar{1}$0)

with the crystal in the Laue position. In the Laue position the x-rays
pass through the crystal in the diffraction process. This work along
with my precise comparison of Laue and Bragg reflection angles using a
double crystal spectrometer included in Brown's thesis seemed to estab-
lish the validity of using macroscopic density data in computing the
grating constant d. A short time later an experiment with the photo-
graphic spectrometer cast considerable doubt on the conclusiveness of
our above mentioned results.

The photographic spectrometer used by Brown consisted of a fine
slit located at a known distance from a photographic plate. The thin
calcite crystal mounted in the Laue position was placed adjacent to the
slit and on the x-ray tube side as shown in the accompanying sketch.
(The drawing is not to scale) With this arrangement very sharply
defined lines were obtained and the angles thus measured were in com-
plete agreement with values obtained by surface reflection.

A short time after the conclusion of the double crystal spectro-
meter investigation the same thin calcite crystal was mounted in the
photographic spectrometer in the position shown in Fig. 1, i.e. with the

CALCITE

$\psi-\theta$

θ_2

d_1

2θ

A_2

SLIT

θ_1'
θ_2'

B_1

2θ

d_2

$\frac{\pi}{2}-\psi-\theta$

A_1

ψ

FIG.1
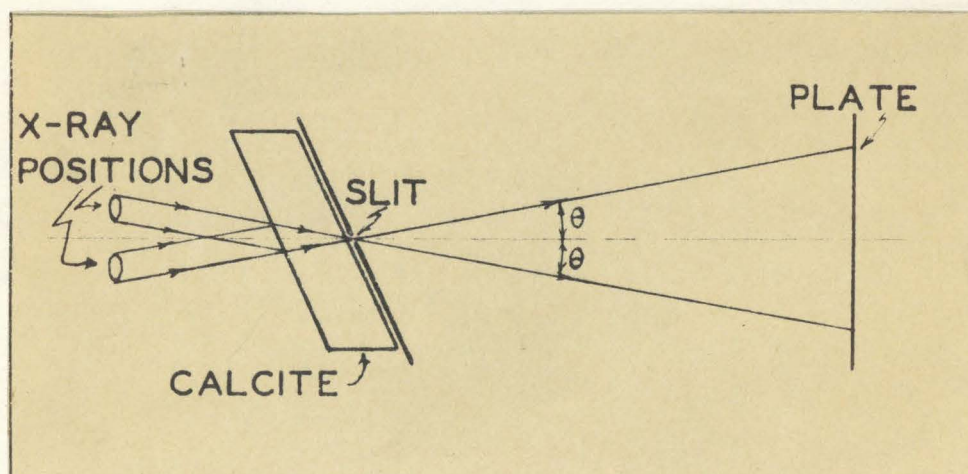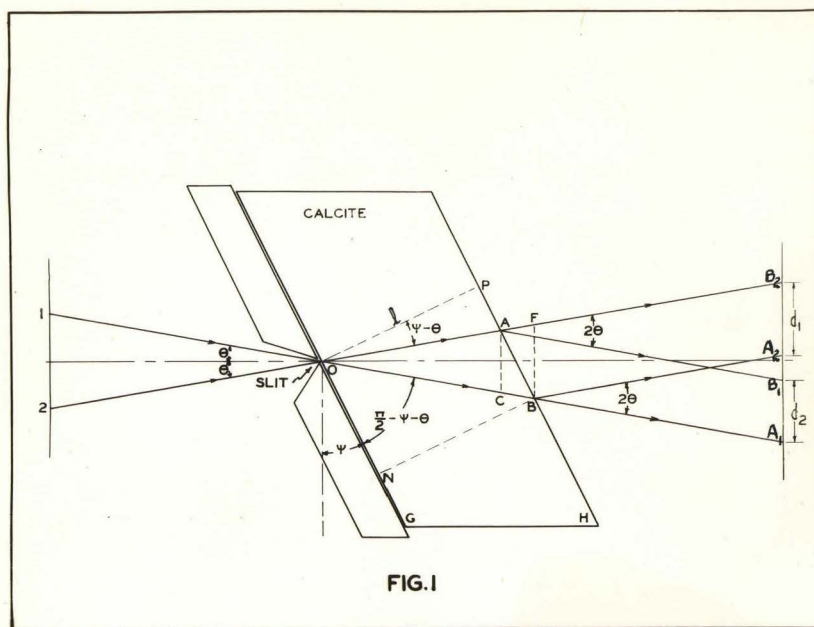
slit between the crystal and the x-ray tube. The crystal was oriented

so as to allow planes parallel to the cleavage plane GH to reflect the

wavelengths of the Mo $K\alpha_1$ and $K\alpha_2$ lines to the photographic plate. In

order to secure a complete photograph two exposures were taken, one with

the x-ray tube at position 1, the other with the x-ray tube at position

2. In each case half of the photographic plate was shielded to prevent

the direct radiation from striking the film. Consider then what one

should expect to obtain on the photograph with this arrangement. The

radiation from the tube passes through the slit O and through the crystal

to the point B. With the angle θ properly chosen, the radiation of wave-

length λ undergoes multiple reflection in the triangular region OBA

according to the Bragg equation. One should expect, therefore, if the

crystal is entirely homogeneous, to obtain by selective reflection of

monochromatic radiation a broad line of width d_1 or d_2 depending upon the

position of the x-ray tube. The values of d_1 and d_2 may be expressed in terms of the Bragg angle Θ, the characteristic angle of calcite ($\Psi = \alpha - \frac{\pi}{2}$, where α is the dihedral angle of calcite), and the thickness l of the crystal. From the figure

$$\overline{AC} \equiv d_2 = 2\,\overline{OA}\,\sin\Theta$$

$$\overline{FB} \equiv d_1 = 2\,\overline{OB}\,\sin\Theta$$

$$\overline{OA} = \frac{\overline{OP}}{\cos(\Psi - \Theta)}, \qquad \overline{OB} = \frac{\overline{BN}}{\sin\left[\frac{\pi}{2} - (\Psi + \Theta)\right]} = \frac{\overline{BN}}{\cos(\Psi + \Theta)}$$

$$\overline{OP} \equiv \overline{NB} \equiv \ell$$

and hence

$$d_1 = \frac{2\,\ell\,\sin\Theta}{\cos(\Psi - \Theta)}$$

and

$$d_2 = \frac{2\,\sin\Theta}{\cos(\Psi + \Theta)} \ .$$

The results of the experiment showed, however, not two broad lines for the α doublet, but four distinct lines, i.e., a pair for each of the two members of the wavelength doublet. These may be seen in the reproduction of Fig. 2. These pairs were attributed to enhanced reflections at the front and back surfaces of the crystal. The separations of these lines were measured and although the α doublet separation agreed with the value calculated from the Bragg equation the other separations did not correspond precisely to the values of d_1 and d_2 calculated from the above formulas. Another photograph taken with the plate nearer to the slit showed the expected change in the separation of the two different wavelength components α_1 and α_2. The pairs of lines of a given wavelength also showed a slight change in separation approaching a little

FIG. 2

$\alpha'_1 \alpha_1 \alpha_2 \alpha_2'$
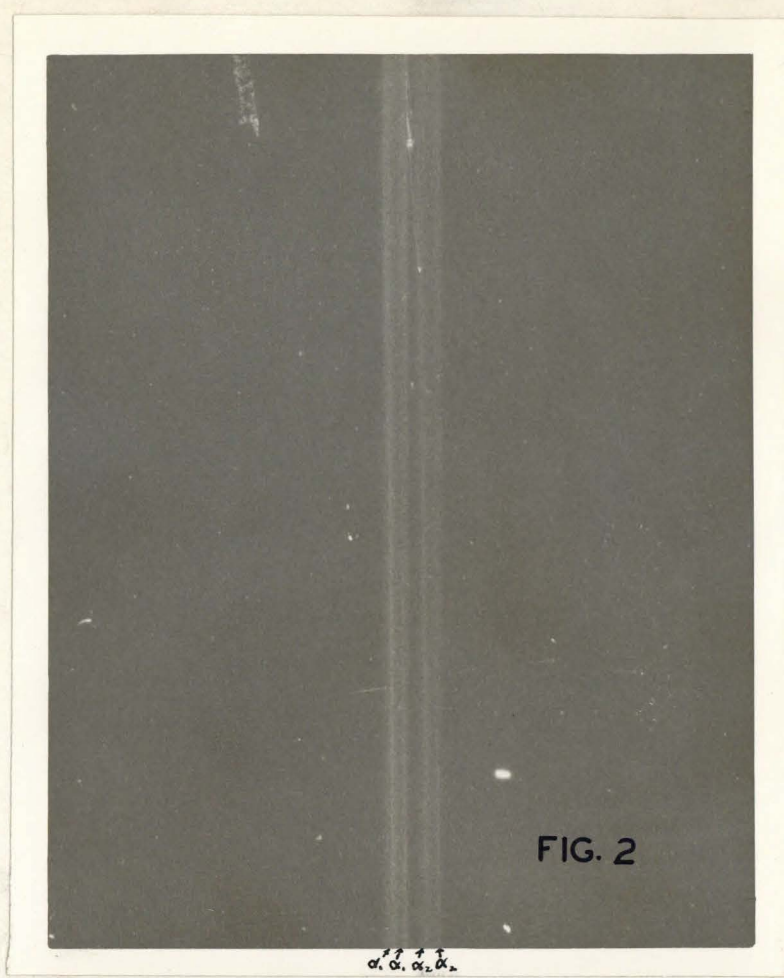
nearer to the calculated values d_1 and d_2. Extrapolating back geometrically to the separations to be expected at the crystal, the values $d_1 = 0.0234$ cms and $d_2 = 0.0221$ cms were obtained. The calculated values for this crystal of thickness 0.9 mm were $d_1 = 0.0232$ cms and $d_2 = 0.0217$ cms, in good agreement with the extrapolated values.

From this one seems forced to conclude (I) that the two beams forming a pair of separation d_1 or d_2 proceed as though they were reflected only from the front and back surfaces of the crystal and not from the interior, (II) that these two components are not reflected at

quite the same angle and form two beams which converge slightly as they leave the crystal. Subsequent work has shown this to be true in varying degrees of many other cleaved samples of crystal also. More or less periodic changes in intensity along the length of the lines were also observed, an effect which I have never before seen reported. All these peculiarities at first contribute to a suspicion that interference may explain the absence of intensity between the components $A_1 B_1$ and $A_2 B_2$ (see Fig. 1) as well as the fluctuations of intensity along the length of the lines. If this were the case we could not conclude that the interior of the crystal had not played a part in forming the interference pattern, but merely that the x-rays at certain points in the pattern were extinguished by unfavorable phase relation. Careful experiments were therefore tried to see if by cutting off parts of the radiation proceeding from the reflecting triangular region OAB the remaining intensities would be modified. For this purpose carefully constructed subsidiary screens were inserted by means of micrometer screws so as to cover regions near A or B at will. These screens could even be so arranged that only reflection occurring in the interior regions of the crystal could form lines on the plate. The intensities in the pattern were not modified by cutting off various portions of the region OAB which seems to indicate that components $A_1 B_1$ are really reflected only from the front and back surfaces and are probably an effect of enhancement caused by surface disturbance of the lattice. Moving the x-ray source up or down parallel to the length of the slit led to the conclu-

sion that the fluctuations of intensity along the length of the lines
must be associated with definite conditions at fixed points on the
crystal. While I feel that not enough is yet known about these peculiar-
ities of calcite reflection it may at least be concluded from the above
that there is grave doubt whether even in the Laue type of reflection
the interior planes of the crystal play an important part unless by some
shielding device such as just described the very weak reflection between
components $A_1 B_1$ or $A_2 B_2$ is perforce the only radiation permitted to be
observed. The very weak lines formed in this way proved unfortunately
to be rather ill defined and unsatisfactory for a precision determination.
The slight convergence of the pairs of beams $A_1 B_1$ or $A_2 B_2$ together with
the generally more or less erratic character of this entire behavior
above described made it look as though a _statistical_ method which would
average out the differences between different samples of calcite and the
different behavior in different regions of one sample of calcite was
much to be desired.

The work on macroscopic pieces of calcite in Laue reflection
may thus be quite appropriately criticized, (I) as really failing to
measure the interior grating constant of the crystal which is involved
in the density determinations, (II) as being too highly dependent on
peculiarities of individual crystals or individual regions in one crystal.

The difficulties involved in the above experiments pointed the
way to the solution of the problem. Since one is apparently restricted
to investigations of a very superficial layer when using macroscopic

calcite either in Laue or Bragg reflection, the answer must lie in the results obtained from finely powdered calcite. It was pointed out above that a volume of only 4×10^{-4} cc out of a total crystal volume of 10 cc was actually used in ordinary work with macroscopic crystals. If, however, one investigates the x-ray properties of crystals of size 10^{-4} cms on a side it is obvious that a result truly representative of the entire sample is obtained, since the depth of penetration is of the order of the dimension of the individual crystals. Although powdered crystal technique properly lies in the realm of crystal structure determination where great accuracy is not ordinarily required, the methods are capable, under special circumstances, of high precision. The research described in the following pages deals with a precise determination of the properties of powdered calcite related to the problem of establishing the validity of the x-ray crystal method for determining "e". There are essentially two distinct parts to the research, namely, the determination of the density of powdered calcite, and the determination of the angles of x-ray reflection for a number of atomic planes. From the latter one may calculate the lattice parameters for powdered calcite and from these establish a direct comparison between the grating constant of the cleavage planes for macroscopic and microscopic calcite.

To put the conclusions as to the value of "e" quite beyond criticisms of the sort here discussed it is important that the density of the same identical powdered calcite, a representative sample of which is used for the diffraction experiment, should be determined. This avoids

two possible criticisms. I. That the density of the calcite used for diffraction might be different from the mean density of some macroscopic sample measured. II. That the effect of powdering might change the density. This last possibility cannot be safely neglected in a really critical consideration of the problem, for it is not impossible for instance that some form of periodic internal strain distribution may exist in the interior of a macroscopic piece of calcite which upon powdering to sufficient fineness might be released thus changing the volume or shape of the unit cell by a slight amount. The powder method here reported together with the pycnometric density determination made directly on the same powder samples conclusively avoids all of the above objections. The shape and absolute size of the unit calcite cell in the tiny powder grains is directly determined by the experiment.

Pycnometric Determination of the Density of Powdered Calcite

The weighings were made on an analytical balance, the weights for which I carefully calibrated against a one gram standard obtained from Dr. Swift of the Chemistry Department. The pycnometer was of conventional design with included thermometer.

The density of the water used in filling the pycnometer was checked by weighing a known volume of water, measured by means of a standardized pipette. The ordinary distilled water available in the laboratory was found to have a density approximately 0.08 per cent lower than that given in the Physics and Chemistry Handbook tables.

This water was re-distilled in an all glass still and then boiled to remove occluded gas. The following table shows the agreement between measured densities at various temperatures and those listed in the tables. In all weighings corrections were made for the effect of buoyancy of air.

Measured Density ρ_1	Density (Tables) ρ	Temperature $^{\circ}$C	Deviation $\rho - \rho_1$
0.99856	0.99790	21.4	−0.00066
0.99756	0.99793	21.3	+0.00037
0.99824	0.99795	21.2	−0.00029
0.99804	0.99793	21.3	−0.00011
0.99796	0.99801	20.9	+0.00005
0.99752	0.99799	21.0	+0.00047

$$\sum (\rho - \rho_1) = +0.00017$$

$$\text{Average deviation} = \frac{\sum (\rho - \rho_1)}{6} = 0.00003$$

The results of these measurements allow one to assume the density values given in tables to be applicable to this re-distilled water.

The density of the calcite crystals whether macroscopic or microscopic was determined as follows: let W be the weight of the empty pycnometer bottle and V its volume determined by weighing the bottle filled with water of known density at a given temperature. Let W_1 be the weight of the bottle plus the weight of the calcite crystals

and W_2 the weight of the bottle plus the weight of crystals plus the weight of water necessary to fill the pycnometer bottle to the fiducial mark. Then if δ is the density of air, the true weight W_c of the calcite is given by

$$W_c = W_1 - W + \delta \left\{ \frac{W_1 - W}{2.7} - \frac{W_1 - W}{8.5} \right\}$$

where the first and second terms in the bracket are, respectively, the corrections for the volumes of air displaced by the calcite and by the weights added for balance in this weighing. The density of calcite is taken to a good enough approximation as 2.7 and that for the weights as 8.5. The density δ of air was taken as 0.0011 gms/cc. The weight W_3 of the water added is given similarly by

$$W_3 = W_2 - W_1 + \delta \left\{ \frac{W_2 - W_1}{1} - \frac{W_2 - W_1}{8.5} \right\}$$

where the first term in the bracket is the buoyancy correction for the volume of air displaced by the added water. The volume of water added is given by

$$V_{H_2O} = \frac{W_3}{\rho_{H_2O}}$$

where ρ_{H_2O} is the density of the water. The volume V_c of the calcite in the bottle is evidently the total volume V minus the volume V_{H_2O}, i.e.

$$V_c = V - V_{H_2O}$$

from which one obtains at once the density of calcite as

$$\rho_c = \frac{W_c}{V_c} \qquad .$$

The values of V and W for the pycnometer bottle were

$$V = 25.5120 \quad \text{at } 20^\circ \text{ C}$$

$$W = 27.3605 \text{ gms.}$$

As a check on Bearden's[3] value for the density of calcite, I determined the density of a group of calcite crystals ranging in volume from 1 cubic mm to approximately 10 cubic mm. Three determinations were made with the following results

Approx. Weight of Sample Used gms.	Temp. $^\circ$C	Density ρ_{mc}
12	20	2.7108
12	20	2.7107
12	20	2.7110

Six determinations were then made on calcite powder obtained by grinding calcite crystals of the size measured above in a mortar. The average size of the calcite powder crystals was estimated at 2×10^{-4} cms on a side by means of a microscope. In filling the pycnometer bottle containing the powdered calcite with water it was found that pre-evacuation of air by means of a vacuum pump decreased the tendency for small air bubbles to be trapped by the powder. Stirring by rotation of the bottle

during filling was also resorted to. The following tabulation gives
the data obtained

Weight of Sample Used gms (approx)	Temp °C	Density ρ_{pc} gms/cc
13.5	20	2.7097
21.3	20	2.7094
12.0	20	2.7106
10.8	20	2.7105
10.5	20	2.7114
10.5	20	2.7097

The probable values for the density ρ_{pc} of powdered calcite
and ρ_{mc} of large calcite with Bearden's[3] value ρ_B for large
calcite crystals are given below

$$\rho_{pc} = 2.71022 \pm 0.00035 \text{ gm/cc}$$

$$\rho_{mc} = 2.71083 \pm 0.00019 \text{ gm/cc}$$

$$\rho_B = 2.71030 \pm 0.00003 \text{ gm/cc} \quad .$$

Identification of the Planes of Calcite Taking Part in Reflection

The original attempt in checking the x-ray reflection angles
for powdered calcite was based on the reflections from the planes having
indices $1\bar{1}0$ with reference to the cleavage cell. The relation between
these planes and the 100 cleavage planes is shown in the accompanying
sketch which represents a cross section made by a cut normal to two
cleavage faces. The angles of reflection for the $1\bar{1}0$ planes using Mo K

radiation were checked by Brown[4] using macroscopic calcite and found to be entirely consistent with values calculated from the accompanying figure using the conventional value (1) of

$$d_{100} = 3.02904 \text{ A} \quad \text{and}$$

$$\alpha = 105° \ 3' \ 29'' \quad \text{Bearden[3]} .$$
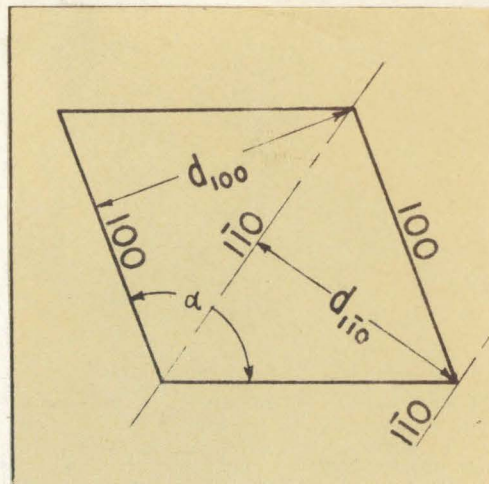
The relation between d_{100} and $d_{1\bar{1}0}$ is readily found to be

$$d_{1\bar{1}0} = \frac{1}{2} \frac{d_{100}}{\cos \frac{\alpha}{2}}$$

from which $\quad\quad d_{1\bar{1}0} = 2.4895 \text{ A}$.

In order to obtain the greatest precision possible with a Seeman-Bohlin spectrograph described elsewhere in this paper it is necessary that the Bragg equation

$$n \lambda = 2 d \sin \Theta$$

be satisfied for the above value of $d_{1\bar{1}0}$, a value of Θ slightly less than 90°, in order to give high precision, an order n (not too high because of intensity considerations), and a value for the wavelength λ corresponding to a characteristic line of an element available as

target material for an x-ray tube. A survey of the elements from Fe atomic number 26 to Ge atomic number 32 for their entire K series showed Ni with atomic number 28 to be the only possibility. Elements with atomic numbers less than 26 have a K series whose wavelengths are so long as to make their use difficult because of absorption and those with atomic numbers greater than 32 impossible because of the high order necessary to satisfy the Bragg equation at the desired angle.

The deliberate choice of nickel as a target automatically fixes the theoretical position of the $K \alpha_1$, $K \alpha_2$ lines on the photographic film reflected from the $1\bar{1}0$ planes. There is, however, the possibility of other planes having grating constants near $d_{1\bar{1}0}$. In order to correlate the complete experimental data with the structure of calcite one must determine theoretically the possible planes of reflection for the angular range covered by the photographic film. These considerations deal with the construction of the reciprocal lattice for calcite. The method of obtaining this lattice is described below.

It is customary for x-ray spectroscopists to use the natural rhombohedral cleavage cell of calcite as a basis for their lattice notations. This point of view was taken in the above paragraphs. The fundamental directions for the three reference vectors from a crystallographic point of view is not along the edges of a natural cleavage cell but in the directions of lines drawn from a Ca atom at the acute vertex of a cleavage cell to each of the Ca atoms in the center of three cleavage faces[5].

These three vectors $\bar{a}_1$, $\bar{a}_2$, and $\bar{a}_3$ so defined form the basis for the rhombohedral crystallographic system. These vectors are of equal length and make an angle γ with respect to each other.
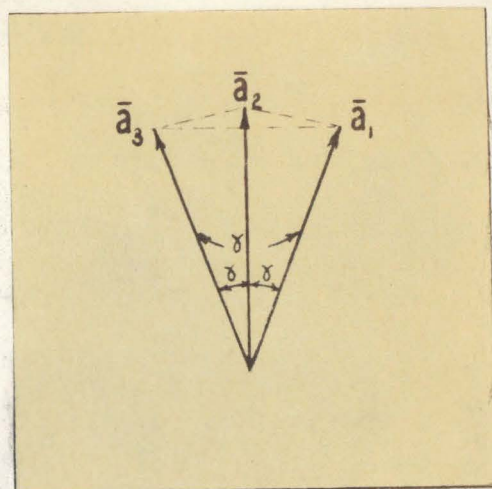

In this system the atoms are located as follows:

Atom	Number	Locations
Ca	2	$(000), (\frac{1}{2}\frac{1}{2}\frac{1}{2})$
C	2	$(\frac{1}{4}\frac{1}{4}\frac{1}{4}), (\frac{\bar{1}}{4}\frac{\bar{1}}{4}\frac{\bar{1}}{4})$
O	6	$\pm(\frac{1}{4}\frac{1}{4}\frac{1}{4} + \{u\,\bar{u}\,0\}), u = 0.25$.

This unit cell contains two molecules. The cleavage cell contains 32 molecules.

For convenience in constructing the reciprocal lattice, the rhombohedral system is transformed to a hexagonal system. Let the reference vectors in the hexagonal system be denoted by $\bar{A}_1$, $\bar{A}_2$, $\bar{A}_c$. The hexagonal system
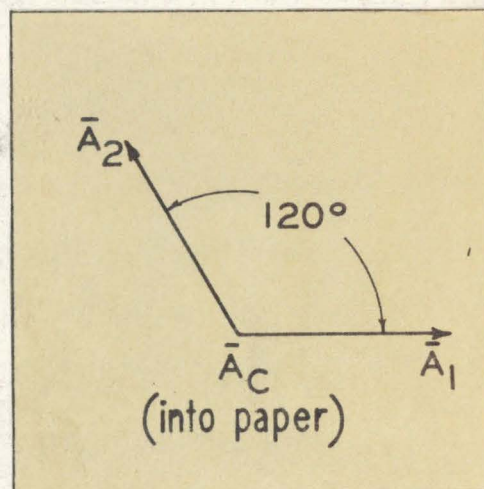
is defined by the transformation equations

$$\bar{A}_1 = \bar{a}_2 - \bar{a}_3$$

$$\bar{A}_2 = \bar{a}_3 - \bar{a}_1$$

$$\bar{A}_c = \bar{a}_1 + \bar{a}_2 + \bar{a}_3 \ .$$

The inverse transformation equations are

$$\bar{a}_1 = \frac{1}{3}\left\{ - \bar{A}_1 - 2\bar{A}_2 + \bar{A}_c \right\}$$

$$\bar{a}_2 = \frac{1}{3}\left\{ 2\bar{A}_1 + \bar{A}_2 + \bar{A}_c \right\}$$

$$\bar{a}_3 = \frac{1}{3}\left\{ - \bar{A}_1 + \bar{A}_2 + \bar{A}_c \right\}.$$

The relation between the dimensions of the two systems is given by the equations

$$A_c^2 = \bar{A}_c \cdot \bar{A}_c = 3a_1^2 \left\{ 1 + 2\cos\gamma \right\}$$

$$A_1^2 = A_2^2 = \bar{A}_1 \cdot \bar{A}_1 = 2a_1^2 \left\{ 1 - \cos\gamma \right\}.$$

The equations

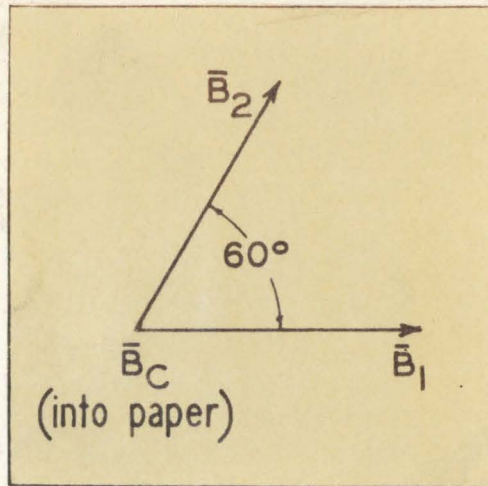$$\bar{B}_1 = \frac{\bar{A}_2 \times \bar{A}_3}{\bar{A}_1 \cdot \bar{A}_2 \times \bar{A}_c}$$

$$\bar{B}_2 = \frac{\bar{A}_3 \times \bar{A}_1}{\bar{A}_1 \cdot \bar{A}_2 \times \bar{A}_c}$$

$$\bar{B}_c = \frac{\bar{A}_1 \times \bar{A}_2}{\bar{A}_1 \cdot \bar{A}_2 \times \bar{A}_c}$$

define a lattice having axes $\bar{B}_1$, $\bar{B}_2$ and $\bar{B}_c$ which is reciprocal to the

hexagonal lattice. The
expression $\bar{A}_1 \cdot A_2 \times A_C$
is the volume of the crystal
unit in the hexagonal system.
The orientation of the recip-
rocal axes is shown in the
accompanying sketch. From
the above relations

$$B_1 = \frac{2}{\sqrt{3}} \quad \frac{1}{A_1} = B_2$$

and $\quad B_C = \frac{1}{A_C}$.

The convenience of a reciprocal lattice in locating the
reflecting planes is made clear in the following discussion.

One may consider the Bragg equation $\lambda = 2 d \sin \theta$ as a
vector equation by writing it as

$$2 \sin \theta (\frac{\bar{1}}{\lambda}) = (\frac{\bar{1}}{d}) .$$

Here d is a generalized grating space which includes the order number
n. The left hand side of this equation is proportional to the momentum
transfer normal to the crystal grating by the reflection of radiation
of momentum $p = \frac{h}{\lambda}$ at the Bragg angle θ. If d is the interplanar
distance for planes of Miller indices H_1, H_2, H_C in the hexagonal system
then the vector $(\frac{\bar{1}}{d})$ represents a line drawn from the origin to the

point in the reciprocal lattice having the coordinates (H_1, H_2, H_c).
Hence, given a wavelength λ, the planes which will reflect this rad-
iation according to the Bragg equation are determined by the intersec-
tions $(H_1 H_2 H_c)$ in the reciprocal lattice at a distance $R = \dfrac{2 \sin \theta}{\lambda}$
from the origin. The vector $\bar{R}$ sweeps out a sphere in the three
dimensional reciprocal lattice having axes $\bar{B}_1$, $\bar{B}_2$, and $\bar{B}_c$ described
above. The problem of determining the reflecting planes for an angle
θ and wavelength λ is thus reduced to finding the intersections of the
sphere of radius R with the intersections $(H_1 H_2 H_c)$ in the reciprocal
lattice. In order to reduce the problem to one of finding intersections
in the plane $\bar{B}_1 B_2$, one calculates the radii of the circles cut out of
the sphere by planes normal to the vector $\bar{B}_c$ for heights nB_c above the
reference plane where n is an integer running from 0 to the greatest
integer in R/B_c. The radii of the circles are given by

$$R_n = \sqrt{R^2 - n^2 B_c^2} \ .$$

The numbers n are the possible values of the index H_c.

Two reciprocal lattices were necessary to determine the planes
taking part in reflections for the range $70^\circ < \theta < 90^\circ$ used in the
experiment. These are shown in Figures 3 and 4. Only a portion of the
lattice need be drawn because of symmetry.

The values $a_1 = a_2 = a_3 = 6.361$ A and $\gamma = 46^\circ 7'$ were taken
from Ewald-Hermann "Strukturbericht" page 293. The scale upon which the

23

FIG. 3

FIG. 4
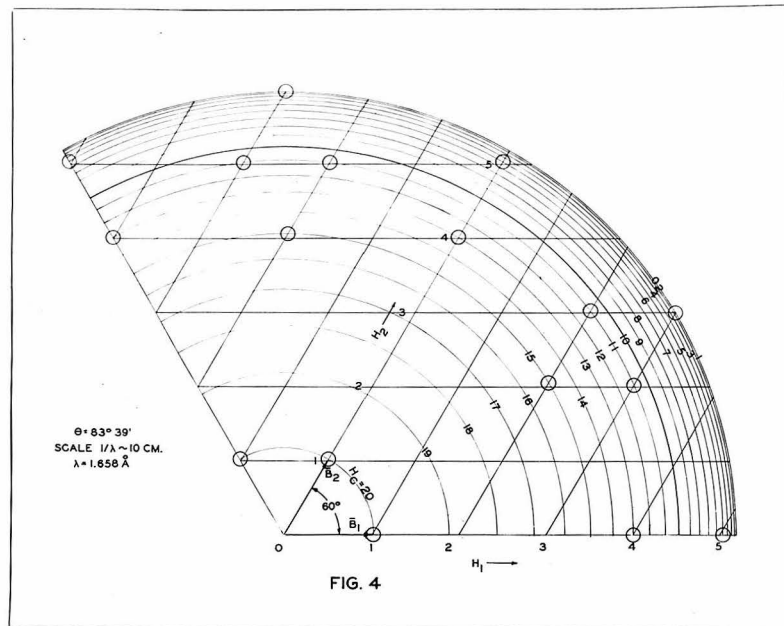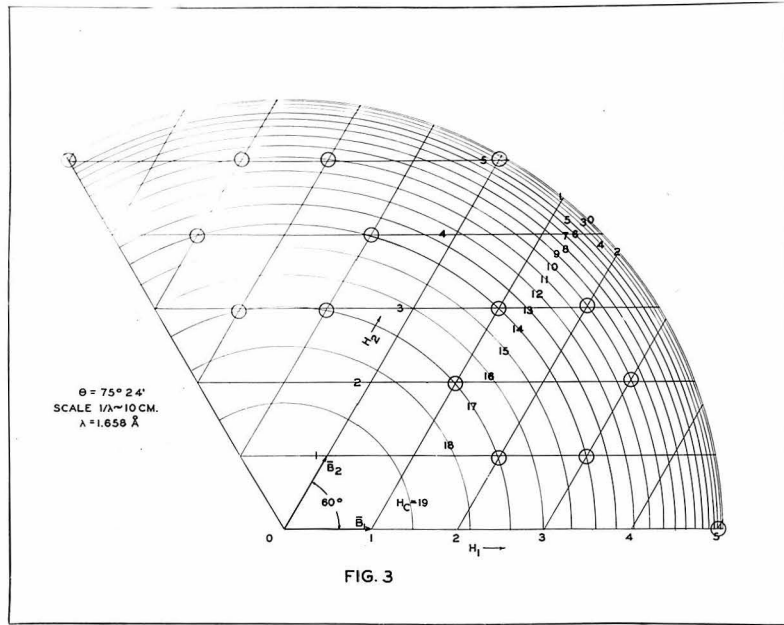
distance a is based is somewhat indefinite, but presumably corresponds to the Siegbahn scale wherein d_{100} (cleavage system) for calcite is defined as $d_{100}= 3.0290$ A at 18° C. For the present application (the identification of the diffractions rings) the fineness of this point need not be stressed. The reciprocal lattice scale was taken for convenience as $\frac{1}{\lambda} \sim 10$ cms. The calculations were based on $\lambda = 1.65835$ A [6] (Siegbahn scale) for the nickel $K\alpha_1$ line. The circles of Fig. 3 correspond to a value of $\theta = 83^{\circ}$ 39' and $R_0 = 19.878$ cms. The calculated values of the reference vectors are

$$A_c = 17.020 \text{ A}, \qquad A_1 = A_2 = 4.983 \text{ A}$$
$$B_1 = B_2 = 3.843 \text{ cms}, \qquad B_c = 0.9744 \text{ cms}.$$

All of the intersections $H_1 \; H_2 \; H_c$ do not produce possible reflecting planes in the rhombohedral system. If $h_1 \; h_2 \; h_3$ are the Miller indices in the rhombohedral system the transformation equations for the indices are analogous to those for the vectors, namely

$$h_1 = \frac{1}{3} \left\{ - H_1 - 2H_2 + H_c \right\}$$

$$h_2 = \frac{1}{3} \left\{ 2H_1 + H_2 + H_c \right\}$$

$$h_3 = \frac{1}{3} \left\{ - H_1 + H_2 + H_c \right\}.$$

Any workable set of indices $H_1 \; H_2 \; H_c$ must yield _integers_ for $h_1 \; h_2 \; h_3$. This fact rules out some of the intersections in the reciprocal lattice.

The ones which yield planes are encircled on the charts.

It is shown in the theory of crystal structures that the grating constant $d_{h_1 h_2 h_3}$ for a set of planes having Miller indices $h_1\ h_2\ h_3$ in a rhombohedral system is given by

$$d_{h_1 h_2 h_3} = \frac{a\sqrt{1 + 2\cos^3\gamma - 3\cos^2\gamma}}{\sqrt{(h_1^2 + h_2^2 + h_3^2)\sin^2\gamma + 2(h_1 h_2 + h_1 h_3 + h_2 h_3)(\cos^2\gamma - \cos\gamma)}}$$

where as before for calcite $a = 6.361$ A and $\gamma = 46^\circ\ 7'$ approximately. The grating spacings for the sets of indices $h_1\ h_2\ h_3$ found by the method described above were calculated by means of this relation, using these constants. These furnish a foundation for identifying the lines observed.

The intensity of reflection from a powdered crystal for a set of planes $h_1\ h_2\ h_3$ is

$$I = K\ P\ f(\theta)\ F^2$$

where K = proportionality constant

P = permutation factor

$f(\theta)$ = a function to take into account the decline of F with θ

and F = crystal structure factor.

Since only a small range of θ is used, we may without serious error omit the function $f(\theta)$ and write

$$I \propto P\ F^2.$$

The expression for the crystal structure factor F is well known[1] and may be written as

$$F = \sum_j f_j\, e^{2\pi i(h_1 x_j + h_2 y_j + h_3 z_j)}$$

where the summation is extended over the various atoms in the crystal cell having coordinates x_j, y_j, z_j. The term f_j is the atomic structure factor the values for which have been plotted as a function of $\frac{\sin \theta}{\lambda}$ by Pauling and Sherman[7]. The values of $f_{ca} = 7.81$, $f_c = 1.60$, and $f_o = 1.85$ for $\theta = 80°$ were obtained from the Pauling and Sherman graphs. These atomic structure factors are a measure of the efficiency of the atoms in scattering x-rays. The atomic coordinates for calcite were listed above as

$$2\ \text{Ca} \quad \text{at} \quad (0\ 0\ 0),\ (\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2})$$

$$2\ \text{C} \quad \text{at} \quad (\tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{1}{4}),\ (\tfrac{\bar{1}}{4}\ \tfrac{\bar{1}}{4}\ \tfrac{\bar{1}}{4})$$

$$6\ \text{O} \quad \text{at} \quad \pm(\tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{1}{4} + \{u\ \bar{u}\ 0\})\quad u = \tfrac{1}{4}.$$

Substituting these values into the expression for F one obtains

$$F = \frac{f_{ca}}{2}\left\{1 + (-1)^{h_1 + h_2 + h_3}\right\} + f_c \cos 2\pi(\frac{h_1 + h_2 + h_3}{4}) +$$

$$+ f_o\left\{\cos 2\pi(\frac{h_1}{2} + \frac{h_3}{4}) + \cos 2\pi(\frac{h_1}{4} + \frac{h_2}{2}) + \cos 2\pi(\frac{h_2}{4} + \frac{h_3}{2})\right\},$$

where f_{Ca}, f_C, and f_O are the respective atomic scattering factors
for Ca, C, and O atoms. The factor P is necessary to take into account
the possible permutations of the indices h_1 h_2 h_3 which yield the same
grating space $d_{h_1 h_2 h_3}$. Any set of planes having the same grating space
will reflect radiation to the same region on the photographic film
and hence the intensity must be weighted by the factor P. The factor
P is taken as the number of ways in which h_1 h_2 h_3 may be taken with
$(h_1^2 + h_2^2 + h_3^2)$ and $(h_1 h_2 + h_1 h_3 + h_2 h_3)$ invariant.

A tabulation of the planes and their grating constants with
expected relative intensities is given below.

Hexagonal Indices $(H_1 \ H_2 \ H_C)$	Rhomb. Indices $(h_1 \ h_2 \ h_3)$	Grating Space $d_{h_1 h_2 h_3}$	Weight Factor P	Structure Factor F	Intensity $I \propto PF^2$
1,2,17	476	0.8532	12	3.66	161
3,1,14	374	0.8528	12	4.38	230
3,2,10	163	0.8557	12	8.04	774
0,5,4	$\bar{2}53$	0.8458	6	11.3	762
5,0,2	$\bar{1}4\bar{1}$	0.8586	6	4.38	115
5,0,$\bar{1}$	$\bar{2}3\bar{2}$	0.8619	6	1.83	20
0,1,20	677	0.8349	6	11.3	762
$\bar{2}$,4,15	357	0.8389	12	0	0
0,4,$\bar{1}\bar{3}$	733	0.8326	6	0	0
$\bar{2}$,5,11	146	0.8338	12	3.66	161
$\bar{5}$,5,5	005	0.8366	6	0	0
3,3,0	$\bar{3}30$	0.8304	6	7.58	343

Theory of Seeman-Bohlin Spectrograph

In order to determine the diffraction angles for various planes
in powdered calcite a powder spectrograph was needed. A Seeman-Bohlin
focussing type of powder spectrograph was chosen because of its sim-
plicity of construction and greater accuracy when used as described
below.

The theory of this focussing type of powder camera is as
follows. Let a photographic film be placed on the arc ASB of a circle,
Fig. 5, approximately
symmetric with respect
to a fine slit at S
and let the crystal
powder be pressed into
an arc CDE diametrically
opposite the slit S.
Consider a divergent
beam of x-rays of wave-
length λ passing through
the slit S and falling
on the crystal powder at
CDE. Since the crystal
powder contains a large
number of tiny crystals
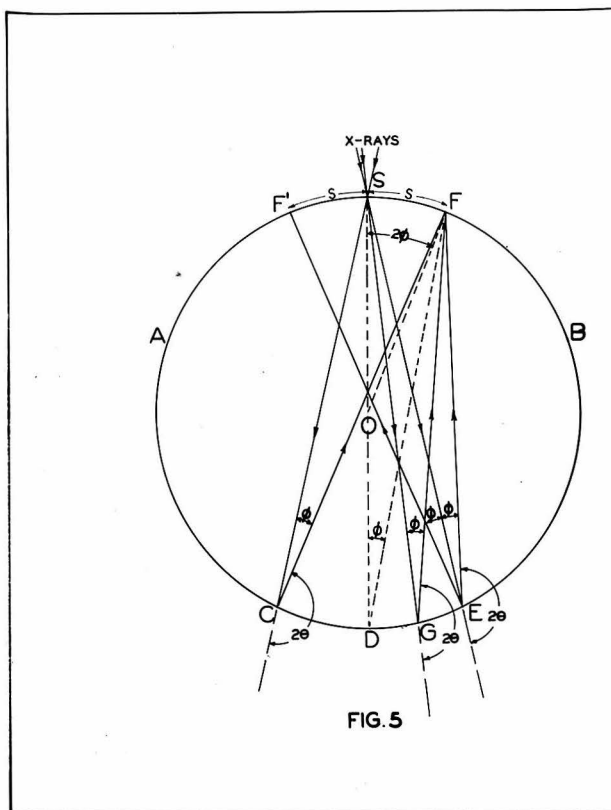randomly oriented there

FIG. 5

will be some of the crystals properly aligned, irrespective of where they lie on the arc CDE, to diffract the x-rays of wavelength λ from a given set of planes of grating space d to a particular point F according to the Bragg equation $\lambda = 2\ d\ \sin\ \theta$, where θ is the angle which the incident and diffracted rays make with the atomic plane normal to the lattice distance d. That the diffracted rays are brought to a focus at F is evident by considering the rays SC and SG. For diffraction, the angles SCF and SGF must be equal to $180^\circ - 2\theta$ and hence they subtend the same arc on the circle, namely SF. Obviously there will be crystals also oriented in such a way as to diffract the x-rays of wavelength λ to the point F' such that the arcs F'S and SF are equal. When used in this way the spectrograph gives a photograph which is symmetric with respect to its center. This is a decided advantage, since the distance between corresponding lines may be more accurately measured than the distance from the slit to a single line.

Let O be the center of the circle, then by geometry the angle SOF is equal to $2\ \emptyset$. If R is the radius of the camera, the arc SF = s is given by

$$s = 2\ R\ \emptyset$$

But $\emptyset = 180^\circ - 2\ \theta$ so that

$$s = 2\ R(180 - 2\ \theta)$$

and $\theta = 90^\circ - \dfrac{s}{4R}$.

Substituting this value of θ into the Bragg equation one obtains

$$(1) \qquad \lambda = 2\,d\,\sin(90^\circ - \frac{s}{4R}) = 2\,d\,\cos\frac{s}{4R}.$$

By differentiation

$$(2) \qquad d\lambda = -\frac{2d}{4R}\sin\frac{s}{4R}\,ds\,.$$

Dividing (2) by (1) gives

$$(3) \qquad \frac{d\lambda}{\lambda} = -\frac{\tan\frac{s}{4R}}{4R}\,ds = -\frac{\phi}{2}\tan\frac{\phi}{2}\frac{ds}{s}.$$

From equation (3) one sees that with a small angle ϕ the relative error in determining the wavelength λ, or, what amounts to the same thing, if λ be considered known, the relative error in determining d, is considerably less than the error made in measuring the arc length s. Even for $2\phi = \pi/2$, $\phi/2 = \pi/8$ $\frac{d\lambda}{\lambda} \cong -\frac{1}{7}\frac{ds}{s}$. Thus in this region a precision of one per cent in measuring the distance s allows a precision in λ of the order of one-tenth of one per cent.

A detailed discussion of the errors introduced by vertical divergence of the beam, slit width, thickness of powder sample, shrinkage of film, and errors in measurement of camera radius has been given by Cohen[8].

Cohen finds for a height h of vertical illumination of the powder sample, a fractional error in the arc length s of amount

$$\frac{\Delta s_h}{s} = \frac{1}{2}\left(\frac{h}{4R}\right)^2\frac{\tan\phi}{\phi}.$$

The arc 2s is independent of the slit width since a widening of the slit produces only a symmetrical broadening of the lines. The effect of a finite thickness t of powder is to produce an error

$$\frac{\Delta s_t}{s} = \frac{t \tan \emptyset}{s} = \frac{t}{2R} \frac{\tan \emptyset}{\emptyset} \ .$$

The effect of shrinkage of film and errors in determination of radius R may be included in

$$\frac{\Delta s_R}{s} = \frac{\Delta R}{R} \ .$$

The total fractional error in s may then be written as

$$(4) \quad \frac{\Delta s}{s} = \frac{1}{2} \left(\frac{h}{4R}\right)^2 \frac{\tan \emptyset}{\emptyset} + \frac{t \tan \emptyset}{2R\emptyset} + \frac{\Delta R}{R}$$

$$= \frac{1}{2} \left(\frac{\tan \emptyset}{\emptyset}\right) \left\{ \left(\frac{h}{4R}\right)^2 + \frac{t}{R} \right\} + \frac{\Delta R}{R} \ .$$

The evaluation of this expression for the conditions used in this experiment will be given later.

Construction of a Seeman-Bohlin Spectrograph

In addition to the necessary theoretical details of the Seeman-Bohlin spectrograph mentioned above one must also consider the problem of making the scattering in the spectrograph as small as possible in order to secure sufficient contrast between the "lines" and background on the photograph.

Scattering from the walls of the spectrograph may be reduced to a minimum by using a material such as lead which has a large ratio for its true absorption to its scattering. In order to reduce the scattering due to the air, the spectrograph was designed so that it could be evacuated.

The cylindrical part of the vacuum spectrograph containing the slit was made as follows. A piece of iron pipe approximately 3 inches long and 7 1/2 inches in diameter was turned inside and out on a lathe. The inner surface was then tinned and a lead lining about one quarter inch thick cast onto it, using a solid concentric core of the proper radius. A 1/2 inch radial hole was then drilled in one side of the cylinder midway between top and bottom. The outer surface surrounding the hole was milled off flat to enable the shoulder of the slit plug to be fitted firmly against the cylinder by means of four tap screws. A detail of the slit plug is shown in Fig. 6. The head cylinder B containing a cap for fastening to the spectrograph cylinder fitted snugly into a lead cylinder of 1/2 inch outside diameter. This plug assembly was then fastened to the spectrograph cylinder and the inside turned to the finish radius on a lathe. The cylinder B was then withdrawn to the position shown in the drawing. This forms a snout to shield the photographic film from the scattering from the edges of the slit. The pin hole slit, approximately 1/2 mm in diameter, was made by deepening the taper hole already in the plug B. This method of turning
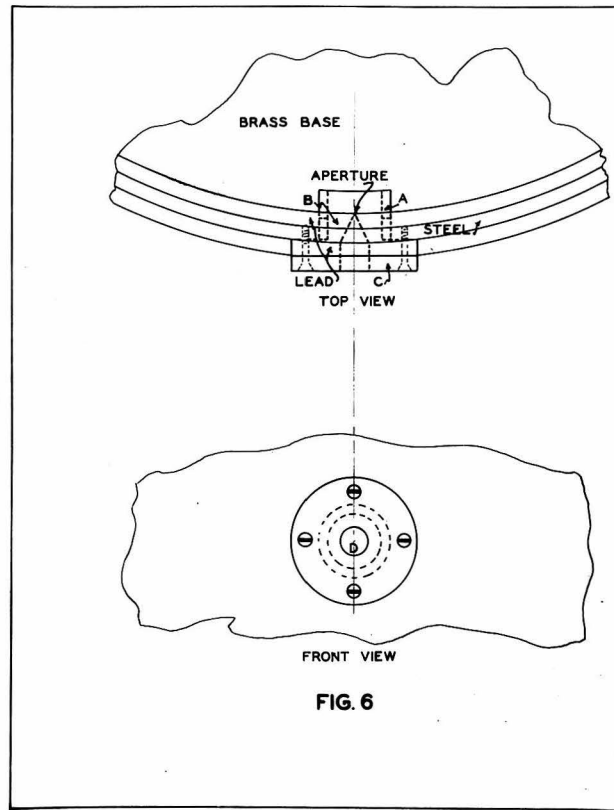
FIG. 6

the plug in place insures that the slit be on the circle. The slit

was made vacuum tight by clamping a cellophane window 0.002 inch

thick between the plug cap and the brass cap C and painting the joints

with glyptal. The cylinder was fitted into a groove turned into a

tinned brass bottom plate. This joint was made vacuum tight by means

of soft wax. The bottom plate was also fitted with a pumping out

connection. The top plate of the spectrograph was similar to the

bottom. The groove was fitted with a rubber gasket instead of wax to facilitate loading the camera. No clamping screws were necessary since the atmospheric pressure was sufficient to squeeze the thin gasket to form a vacuum joint. The film clamp was made out of a sheet of phosphor bronze with a long rectangular hole cut in it to allow the x-radiation to strike the film. This clamp was permanently fastened at one end with screws and contained a slot and a large headed clamping screw at the other end. A photograph of the spectrograph is shown in Fig. 7. The spectrograph was made light tight by placing a small piece of black paper over the slit opening D and by arranging the pumping

FIG. 7

out connection with a right angle bend and long length of rubber tubing before connecting to the manometer. It should be mentioned that the above type of construction wherein the film is placed inside a cylinder instead of on the outside eliminates the necessity of auxiliary shielding.

The diameter of the spectrograph was measured with micrometer calipers at a number of places around the periphery and along its height. The greatest deviation from uniformity was one part in 7000. The mean value of the diameter was

$$D = 6.905 \text{ inches.}$$

The Nickel Target X-ray Tube

For reasons already mentioned a nickel-target x-ray tube was needed for supplying the radiation to the Seeman-Bohlin spectrograph.

In order to reduce the necessary exposure time required for a photograph, a thin windowed x-ray tube was needed. The use of a thin window reduces the loss due to absorption in the glass and is an important item for x-rays as soft as Ni K radiation. The construction of a long narrow x-ray tube also allows one to place the spectrograph slit nearer the target and thus gain a considerable factor in intensity.

The nickel target was obtained by nickel plating a copper target from a commerical tube. The cathode assembly also was of commercial design. I am indebted to Mr. Clancy of this Institute whose

FIG. 8

skill in glass blowing made possible the
construction of this tube. The tube was
fitted with a charcoal trap capable of being
immersed in a liquid air bath. The tube was
pumped out with the charcoal at a temperature
of about 350°C. No other outgassing technique
was resorted to. During the several months
it was in use, no ionization of gas was
noticed in the tube. The general details of
the tube may be seen in the photograph, Fig.7.

Experimental Results Obtained with
the Seeman-Bohlin Spectrograph

A photograph was taken with no calcite
in the spectrograph to determine whether the
lead lining produced selective reflection in
the region to be used in the study of the cal-
cite. The exposure time used was the same as
that for the calcite photographs, namely, 10
hours with the x-ray tube working at 22 K.V.
and 10 ma. The resulting photograph is shown
in Fig. 8. By a coincidence, with diffraction
from the lead lattice, the α doublet lines
shown fall very near to where a set of lines
for the calcite should theoretically come.

This is, of course, an obvious disadvantage. In order to eliminate this undesirable feature, several sheets of thin gold foil were pasted over the lead in the region where the incident x-rays impinge. Another photograph then resulted in a blank, showing that the lead "lines" had been eliminated and no new ones added due to the presence of the gold.

A layer of the powdered calcite from the density determination was pressed on to the wall of the spectrograph using a slight amount of collodion as a binder. The thickness of the layer was approximately 1/4 mm. This corresponds to the thickness of the photographic film used.

An exposure of the time and conditions listed above resulted in the presence of several sets of lines on the photographic film. The general background on the film was very heavy and of a mottled character. Although the lines due to the calcite were distinct and readily measurable when the film was examined under strong illumination the contrast was not sufficient to allow photographic reproduction. Attempts to increase the contrast by use of a Cobaltic oxide filter and various operating voltages on the x-ray tube failed. The heavy mottled background is probably due to the reflection of continuous radiation by tiny calcite crystals which are considerably larger than the average. That this is so is strengthened by the fact that superposed on the general line darkening are very intense spots. These spots are attributed to reflections of line radiation from similar "giant" crystals present in the sample with chance orientations such as to satisfy the Bragg equation

for the line radiation. The use of coarser powder also increased the frequency of these coincidences.

The values of the distances 2s between lines for measurements on five different films are tabulated below. Not all of the films contained the same degree of contrast. This resulted in the absence of some of the lines on certain photographs. The starred measurements for the distances 2.19 and 1.10 inches were made from spots only since the general line radiation was not discernible in the strong background.

Tabulation

Film Number	1	2	3	4	5	Mean
	7.05	7.07	7.06	70.5	7.05	7.056
	6.79	6.75	6.75	6.80	6.75	6.768
Distances		5.70			5.67	5.685
2s		5.39			5.30	5.345
in						
inches	3.78	3.79	3.80	3.75	3.76	3.776
	3.30	3.30	3.26	3.29	3.30	3.290
		*2.18	*2.20			*2.190
		*1.10	*1.10			*1.100

The values for $d_{exp.}$ were calculated from this data by the formula

$$d_{exp.} = \frac{\lambda}{2 \cos \frac{2s}{4D}}$$

where D is the diameter of the spectrograph. $D = 6.905$ inches. The wavelength values for the Ni $K\alpha_1$ and $K\alpha_2$ used were

$$\lambda_{\alpha_1} = 1.65450 \text{ A} \qquad\qquad \lambda_{\alpha_2} = 1.65835 \text{ A} .$$

These wavelengths were measured by Eriksson[6] and are based on the convention of Siegbahn

$$d_{100} \equiv 3.02409 \text{ A} \quad \text{at } 18^\circ \text{ C for calcite.}$$

The d_{exp} thus calculated are on the Siegbahn scale. These values are tabulated below along with the associated values of $d_{h_1 h_2 h_3}$ found from the reciprocal lattice constructions and the constants $a = 6.361$ A, $\gamma = 46^\circ 7'$ taken from Ewald-Hermann which are also presumably on the Siegbahn scale. The values of d_{exp} are listed separately for the $K\alpha_1$ and $K\alpha_2$ lines for comparison. The association of the observed lines with their proper plane indices was not difficult since only the stronger lines were observed. Their intensities are in reasonable agreement with the theoretical calculations.

Indices (Crystallographic Rhombohedral)	Calculated $d_{h_1 h_2 h_3}$ A*	Experimental			Deviation Δ $d_{h_1 h_2 h_3} - d_{exp}$
		$d_{exp.\alpha_1}$ A*	$d_{exp.\alpha_2}$ A*	$d_{exp.average}$ A*	
$\bar{3}$ 3 0	0.8304	0.82987	0.82984	0.82986	+0.00054
6 7 7	0.8349	0.83504	0.83510	0.83507	−0.00017
$\bar{2}$ 3 3	0.8458	0.84510	0.84494	0.84502	+0.00078
1 6 3	0.8557	0.85500	0.85472	0.85486	+0.00084

* Siegbahn Scale

The trend of the Δ's leads one to examine the possible errors in $d_{h_1 h_2 h_3}$ and d_{exp}. From the section treating the theory of the Seeman-Bohlin spectrograph we have

$$\frac{\Delta \lambda}{\lambda} = - \frac{\emptyset}{2} \left(\tan \frac{\emptyset}{2} \right) \frac{\Delta s}{s}$$

and

$$\frac{\Delta s}{s} = \frac{1}{2} \left(\frac{\tan \emptyset}{\emptyset} \right) \left\{ \left(\frac{h}{4R} \right)^2 + \frac{t}{R} \right\} + \frac{\Delta R}{R}$$

where

$\emptyset = \pi - 2\theta$ (θ is the Bragg angle)

$s = 2R\emptyset$ (R is the radius of the spectrograph)

t = thickness of powder sample

and h = height of illumination of powder sample.

From the Bragg equation $\lambda = 2d \cos\frac{s}{4R}$ the fractional error in the grating space d is

$$\frac{\Delta d}{d} = \frac{\Delta \lambda}{\lambda} .$$

The largest value of $\emptyset$ (that corresponding to the planes (163)) used is

$$\emptyset = \frac{s}{2R} = 0.5 \text{ radian} \sim 29^\circ$$

The experimental values of h and t are

$$h = 0.5 \text{ inches}$$

$$t = 0.01 \text{ inches} .$$

A conservative estimate for the error ΔR in the radius R may be taken as one half the thickness of the photographic film equal to 0.005 inches. Thus

$$\frac{\Delta R}{R} \simeq \frac{0.005}{7} = 0.0007$$

Substituting these values into $\frac{\Delta s}{s}$ gives

$$\frac{\Delta s}{s} = \frac{1}{2} \left(\frac{\tan 29^\circ}{0.5}\right) \left\{ \left(\frac{0.5}{14}\right)^2 + \frac{0.01}{7} \right\} + 0.0007$$

$$= \frac{1}{2} (1.1) \left\{ 0.0018 + 0.0014 \right\} + 0.0007$$

$$= 0.0025$$

Hence

$$\frac{\Delta d}{d} = -\frac{\phi}{2} \left(\tan \frac{\phi}{2}\right) \frac{\Delta s}{s} = -(0.25)(0.26)(.0025)$$

$$= -16.3 \times 10^{-5}$$

The percentage error in determining $\Delta d/d$ due to these causes is consequently

$$\delta_1 = -\frac{\Delta d}{d} 100 \leqq -0.016\%.$$

An examination of the measurements of 2s previously tabulated leads to an estimated $\frac{\Delta s}{s}$ from this cause of $\frac{\Delta s}{s} \leq \frac{1}{200}$ giving a percentage error δ_2 in d of

$$\delta_2 = \frac{0.065}{200} \times 100 \leqq 0.04\%.$$

Since δ_2 may be either positive or negative while δ_1 is always negative, a liberal estimate of the probable experimental error seems to be 0.05 of one per cent. The agreement between d_{exp} values obtained from the α_1 and α_2 lines substantiates this estimate.

From a general knowledge of the accuracy sought for in ordinary crystallographic work one is led to expect errors of the order of 0.1 of one per cent or more in the constants a and γ as given in Ewald-Hermann. For this reason and because the deviations Δ are greater in cases than my probable experimental error further comparison of the d_{exp} with the $d_{h_1 h_2 h_3}$ will not be made.

A better method which directly relates to the problem in question is to determine a value for the characteristic angle of the calcite cell and a value for the lattice parameter from the experimental data obtained and compare these values with the accepted values for macroscopic calcite.

Since the data for macroscopic calcite is in terms of the cleavage cell notations, the quantities obtainable from the experimental data will also be calculated on the same basis. We thus need an expression for the grating spaces in terms of the cleavage cell parameters. Since the cleavage cell is also a rhombohedron the desired expression is exactly analogous to that for $d_{h_1 h_2 h_3}$ in the rhombohedral crystallographic system, namely,

$$d_{c_1 c_2 c_3} = \frac{C \sqrt{1 + 2\cos^3\beta - 3\cos^2\beta}}{\sqrt{(c_1^2 + c_2^2 + c_3^2)\sin^2\beta + 2(c_1 c_2 + c_1 c_3 + c_2 c_3)(\cos^2\beta - \cos\beta)}}$$

where C = length of an edge of the cleavage rhombohedron

β = characteristic angle of the cleavage cell, i.e. it is the angle between the three reference vectors in the cleavage system

c = index in cleavage system.

The equations for transformation of indices $h_1 h_2 h_3$ to $c_1 c_2 c_3$ are

$$c_1 = 3h_1 - h_2 - h_3$$
$$c_2 = -h_1 + 3h_2 - h_3$$
$$c_3 = -h_1 - h_2 + 3h_3.$$

The cleavage cell in this case contains thirty two molecules. This is the smallest cleavage cell for which all atomic planes of calcite can be properly indexed. X-ray spectroscopists think in terms of a cleavage cell of calcite having only four molecules. This is only for convenience and leads to no difficulty when cleavage planes and planes simply related to the cleavage planes are used. The volume of the true cleavage cell is eight times the volume of the four molecule cell. The distance d_{100} (four molecule cell notation) is repeated twice in the small cleavage cell and four times in the true cleavage cell. Hence d_{100} in the x-ray spectroscopist's notation corresponds to d_{400} in the large cell. The relation between indices $h_1 h_2 h_3$ and $c_1 c_2 c_3$ along with the experimental grating spaces are given below.

Indices $h_1 h_2 h_3$	Indices $c_1 c_2 c_3$	d_{exp} A*
$\bar{3}\ 3\ 0$	$\bar{12},12,0$	0.82986
$6\ 7\ 7$	$4,8,8$	0.83507
$\bar{2}\ 3\ 3$	$\bar{12},8,8$	0.84502
$1\ 6\ 3$	$\bar{6},14,2$	0.85466

* Siegbahn scale.

It was mentioned above that the measurements on $d_{\bar{3}30}$ were between spots on the film because no filled out ring could be discerned. Mention was also made of attributing intense spots on the film to reflections from "giant" tiny crystals in the sample. As a result the experimental data for these planes ($\bar{3}30$) should be discarded since it is not definitely known that these spots are reflections of radiation having a wavelength truly at the "center" of the spectral line. Measurements made on these isolated spots are not strongly inconsistent with those made on reflection which resulted in continuous rings as far as the grating constant determination was concerned. They did however yield some inconsistency in the value of the characteristic lattice cell angle β which is apparently more sensitive to small variations in the separations 2s of these rings. The absence of a filled out ring for the ($\bar{3}30$) reflection is not surprising since the intensity here should be half that to be expected in the case of say the (677) planes

and also because the huge dispersion at the large angle of the $(\bar{3}30)$ ring renders the line very broad and therefore destroys its contrast against the background.

The three remaining values of d_{exp} may be used to determine the characteristic angle β for calcite from the relation

$$d_{c_1 c_2 c_3} = \frac{C \sqrt{1 + 2\cos^3\beta - 3\cos^2\beta}}{\sqrt{(c_1^2 + c_2^2 + c_3^2)\sin^2\beta + 2(c_1 c_2 + c_2 c_3 + c_1 c_3)(\cos^2\beta - \cos\beta)}} .$$

From the three values of d_{exp} three ratios may be formed. For convenience let

$$d_{468} \equiv d_2 , \qquad d_{\overline{12},8,8} \equiv d_3 , \qquad d_{\bar{6},14,2} \equiv d_4 .$$

The three ratios are then d_2/d_3, d_3/d_4, d_2/d_4.

Let $\quad d_i/d_k \equiv b_{ik}$, $\quad c_1^2 + c_2^2 + c_3^2 \equiv m$

and $\qquad\qquad 2(c_1 c_2 + c_1 c_3 + c_2 c_3) \equiv n$.

Taking the ratio then of d_i to d_k one obtains

$$\frac{d_i}{d_k} \equiv b_{ik} = \sqrt{\frac{m_k + \cos^2\beta\,(n_k - m_k) - n_k\cos\beta}{m_i + \cos^2\beta\,(n_i - m_i) - n_i\cos\beta}}$$

Letting $n_k - m_k \equiv a_k$ and $n_i - m_i \equiv a_i$ one obtains

$$\cos^2\beta\left\{ a_i b_{ik}^2 - a_k \right\} + \cos\beta\left\{ n_k - n_i b_{ik}^2 \right\} + \left\{ m_i b_{ik}^2 - m_k \right\} = 0 .$$

The solutions of this equation are given by

$$\cos\beta = \frac{\left\{n_\kappa - n_i b_{i\kappa}^2\right\} \mp \sqrt{\left[n_\kappa - n_i b_{i\kappa}^2\right]^2 + 4\left[a_i b_{i\kappa}^2 - a_\kappa\right]\left[m_\kappa - m_i b_{i\kappa}^2\right]}}{2\left[a_\kappa - a_i b_{i\kappa}^2\right]}.$$

The numerical values of the quantities used in the evaluation of the three values of β are tabulated below.

i	m_i	n_i	$a_i = n_i - m_i$
2	144	256	112
3	272	-256	-528
4	236	-136	-372

$b_{23} = \dfrac{0.83507}{0.85402} = 0.988225$ $\qquad b_{23}^2 = 0.976589$

$b_{24} = \dfrac{0.83507}{0.85486} = 0.976850$ $\qquad b_{24}^2 = 0.954236$

$b_{34} = \dfrac{0.84502}{0.85486} = 0.988489$ $\qquad b_{34}^2 = 0.977111$

$n_3 - n_2 b_{23}^2 = -506.007$ $\qquad m_3 - m_2 b_{23}^2 = 131.371$

$n_4 - n_2 b_{24}^2 = -380.284$ $\qquad m_4 - m_2 b_{24}^2 = 98.590$

$n_4 - n_3 b_{34}^2 = 114.140$ $\qquad m_4 - m_3 b_{34}^2 = -29.774$

$\left[n_3 - n_2 b_{23}^2\right]^2 = 256043$ $\qquad a_3 - a_2 b_{23}^2 = -637.378$

$\left[n_4 - n_2 b_{24}^2\right]^2 = 144616$ $\qquad a_4 - a_2 b_{24}^2 = -478.874$

$\left[n_4 - n_3 b_{34}^2\right]^2 = 13027.9$ $\qquad a_4 - a_3 b_{34}^2 = 143.914$

From which

$$\cos \beta_{23} = - \frac{262.741}{1274.76}$$

$$\cos \beta_{24} = - \frac{197.180}{957.748}$$

$$\cos \beta_{34} = - \frac{59.548}{287.828}$$

giving the values

$$\beta_{23} = 101^{\circ} \ 53' \ 40''$$

$$\beta_{24} = 101^{\circ} \ 52' \ 51''$$

$$\beta_{34} = 101^{\circ} \ 56' \ 24'' \ .$$

The mean value of the angle β is therefore

$$\beta = 101^{\circ} \ 54' \ 18'' \ \pm \ 48'' \ .$$

Bearden[3] obtains the value $\beta = 101^{\circ} \ 54' \ 4''$ for macroscopic calcite with a probable error of less than $10''$.

Having obtained a value for β, values of the parameter C may be obtained from the expression

$$C_i = d_i \ \frac{\sqrt{m_i \ \sin^2\beta \ + \ n_i \ (\cos^2\beta \ - \ \cos\beta \ )}}{\sqrt{1 \ + \ 2 \ \cos^3\beta \ - \ 3 \ \cos^2\beta}} \quad , \ i = 2,3,4$$

using the experimental values of d_i and $\beta = 101^{\circ} \ 54' \ 18''$.

We have from above

$$d_2 = 0.83507, \qquad d_3 = 0.84502, \qquad d_4 = 0.85486.$$

These are expressed on the Siegbahn scale so that the resulting C_i's will also be on the Siegbahn scale.

Numerical values used in the calculations are

$$m_2 = 144 \qquad m_3 = 272 \qquad m_4 = 236$$

$$n_2 = 256 \qquad n_3 = -256 \qquad n_4 = -136$$

$$\sin \beta = + 0.97849 \qquad \cos \beta = - 0.206290$$

$$\sin^2 \beta = + 0.957444 \qquad \cos^2 \beta = + 0.042555$$

$$\cos^2 \beta - \cos \beta = + 0.248845 \qquad \cos^3 \beta = - 0.0087787$$

i	$m_i \sin^2 \beta$	$n_i(\cos^2 \beta - \cos \beta)$	Σ
2	137.8719	63.7043	201.5762
3	260.4248	-63.7043	196.7205
4	225.9568	-33.8429	192.1139

$$1 + 2 \cos^3 \beta - 3 \cos^2 \beta = 0.854778 \quad .$$

The values of C obtained are

$$C_2 = 12.8238 \text{ Å}$$

$$C_3 = 12.8194 \text{ Å}$$

$$C = 12.8159 \text{ Å}$$

giving a mean value of

$$C = 12.8197 \pm 0.0016 \text{ A (Siegbahn Scale)}$$

with

$$\beta = 101^\circ\ 54'\ 18'' \pm 48''\ .$$

We are now in a position to form a comparison between the grating constant d_{100} of the cleavage planes for powdered calcite and the observed d_{100} of macroscopic calcite. For microscopic calcite (remembering that d_{100} is really d_{400} in the 32 molecule cell).

$$d_{400} = \frac{12.8197\ \sqrt{1 + 2\cos^3 101^\circ\ 54'\ 18'' - 3\cos^2 101^\circ\ 54'\ 18''}}{\sqrt{16\sin^2 101^\circ\ 54'\ 18'' + 0}}$$

$$= \frac{12.8197\ \sqrt{0.854778}}{4 \times 0.97849}$$

$$(d_{400})\text{pc} = 3.02823 \text{ A} \quad \text{on the Siegbahn scale.}$$

The corresponding value for macroscopic calcite on the same scale is

$$d_{400} = 3.02904 \text{ A.}$$

In order to make a final comparison between macroscopic and microscopic calcite as it relates to the determination of the electron charge "e" it is necessary to recall that the grating space for the cleavage planes of calcite is given by

$$d = \sqrt[3]{\frac{Me}{2 Q \rho \, \Phi(\beta)}}$$

where M is the molecular weight of calcite, Q the value of the Faraday, ρ the density of calcite, and $\Phi(\beta)$ the volume factor given by

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

The quantities under question are ρ and $\Phi(\beta)$. To establish completely the validity of x-ray crystal methods of determining "e" one must compare the values of these quantities for microscopic and macroscopic calcite.

Bearden[3] who has admittedly done the most precise work on macroscopic calcite recommends the values

$$\beta = 101° \; 54' \; 4" \pm 1" \quad \text{(error not given by Bearden)}$$

$$\rho = 2.71030 \pm 0.00003 \text{ gms/cc.}$$

and $\qquad \Phi(\beta) = 1.09594 \pm 0.00001.$

The results of the powdered calcite investigations are

$$\beta = 101 \; 54' \; 18" \pm 48" \; \text{(Probable error from inner con-}$$
$$\text{sistency of powder data)}$$

$$\rho = 2.71022 \pm 0.00035 \text{ gms/cc/}$$

and $\qquad \Phi(\beta) = 1.09602 \pm 0.00048 \quad .$

The Bragg angle θ of diffrction for the cleavage planes in the first order for powdered calcite may be obtained from

$$\sin \theta = \frac{\lambda}{2\, d_{pc}}$$

for any wavelength λ expressed on the Siegbahn scale. The value of the Cu Kα_1 wavelength has been measured by Wennerlof[9]. He finds

$$\lambda_{\alpha_1} = 1.537395 \quad \text{(Siegbahn scale)}.$$

Hence $\qquad \sin \theta = \dfrac{1.53740}{6.0565}$.

Bearden[10] has measured the same wavelength with a ruled grating. He gives

$$\lambda_g = 1.5406 \times 10^{-8} \text{ cms}.$$

From the expression

$$\lambda_g = 2 \sqrt[3]{\frac{Me}{2\,Q\,\rho\,\Phi(\rho)}} \quad \sin \theta$$

using the values

$$M = 100.078 \pm 0.005$$
$$Q = (2.89270 \pm 0.00021) \times 10^{14} \text{ abs. e.s.u.} \qquad (2)$$
$$\rho = 2.71022 \pm 0.00035 \text{ gms/cc}$$
$$\Phi(\rho) = 1.09602 \pm 0.00048$$

and the above values of $\sin \theta$ and λ_g one obtains

$$e = 4.799 + 0.007 \times 10^{-10} \text{ e.s.u.}$$

Conclusion

The results of this investigation on powdered calcite completely answer the objections commonly raised to the x-ray crystal method of determining "e". The angles of diffraction are representative of the entire powder sample since the depth of penetration of the x-rays into the crystals is of the same order as the size of the tiny crystals. The density determination therefore applies to identically the same calcite as has been used to diffract the x-rays.

The agreement between the density of microscopic calcite and macroscopic calcite as well as the agreement of absolute size and shape of lattice cell for these two is surprising evidence of the permanence of the lattice structure against mechanical maltreatment. Any objections which might be raised to the rigor of the dynamical theory of x-ray diffraction (as opposed to the simple theory of Laue or Bragg) are also invalidated by this work with powdered calcite since the elementary theory for determining diffraction angles must certainly apply to diffraction by crystals so small that the radiation is negligibly extinguished in passing through them.

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