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# Tests of the Validity of X-Ray Crystal Methods of Determining *e*

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The procedure in determining the electronic charge, *e*, from measurements of x-ray diffraction angles and the density of crystals has been criticized on the ground that while the density measurements are averages of a large volume, say 10 cc of crystal, the x-rays are diffracted from a surface layer as determined by "extinction" only about $4\times10^{-4}$ cm thick, a very small fraction of the total volume in an entirely specialized location. Partial answers to this criticism by Y. C. Tu and by Allison and Armstrong have rendered its validity much less probable. The present work with extremely fine powdered calcite samples whose density was determined with a pycnometer closes the question completely, we believe, leaving no ground whatever for the criticism and placing the x-ray determinations of *e* on a very solid experimental foundation. Our work yields a value for *e* of $4.799\pm0.007$ abs. e.s.u. based on the scale of ruled grating wave-lengths in which Cu $K\alpha_1$ has a wave-length (Bearden's value) of $1.5406\times10^{-8}$ cm. Efforts to remove the above objection by studies on macroscopic calcite samples which failed to withstand our own criticisms are described since they emphasize the pitfalls that a conclusive test must avoid. Several new unexplained crystal diffraction effects discovered in this search for a conclusive test are also described. Agreement to one part in six thousand between Bragg and Laue diffraction angles was established for two different sets of Miller indices in macroscopic calcite.

## I. Criticisms of the X-Ray Method of Determining *e*

It now seems highly probable that the excellent and concordant ruled grating measurements[1] of the wave-lengths of a number of characteristic x-ray lines establish in absolute centimeter units a reliable scale of wave-length values which combined with the very precise relative scale of x-ray wave-lengths in terms of Siegbahn's conventional unit fixes the absolute values of all of the carefully measured x-ray lines to a precision of say one part in two thousand. The usual procedure in determining the electronic charge *e* then involves a measurement of the diffraction angle $\theta$ in Bragg reflection from a crystal surface and a computation of the interplanar spacing *d* of the crystal lattice in absolute units by means of the familiar formula (with refractive index correction of Siegbahn)

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

By such methods the absolute dimensions of the crystal lattice may be determined. If, as in the case of calcite, the lattice is not cubic the absolute volume of the unit cell may be determined either (1) by combining the value of *d* with x-ray or optical goniometric measurements on a macroscopic crystal to establish the characteristic angle $\beta$ of the rhombohedron or (2) x-ray determinations of the interplanar spacing may be made for several Miller indices, two being theoretically sufficient to establish the necessary angular relationships. The first mentioned procedure is by far the more common. The absolute volume of the unit cell for calcite generally expressed as $8d^3\Phi(\beta)$ is then combined with a measurement of the macroscopic density $\rho$ of the crystal employed and by means of the formula

$$d=(Me)^{\frac{1}{3}}[2Q\rho\Phi(\beta)]^{-\frac{1}{3}} \quad \text{or} \quad e=2d^3Q\rho\Phi(\beta)M^{-1} \qquad (2)$$

the value of *e* is computed. *M* is the molecular weight of $CaCO_3$; and *Q* the Faraday constant.

### Three criticisms enumerated

(1) Criticisms have been raised from time to time that the macroscopic density which is an average value for a crystal volume of, say, 10 cc may not apply to the extremely thin superficial layer ($5\times10^{-5}$ cm thick in the first order) involved in Bragg reflection. Allison and Armstrong[2] have endeavored to answer this criticism by measuring the reflection angles in different orders up to the fifth where the penetration, they

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[1] The following is far from an exhaustive list of such work: Compton and Doan, Proc. Nat. Acad. Sci. **11**, 598 (1926); J. Thibaud, J. de phys. et rad. **8**, 13 (1927); E. Bäcklin, Inaugural dissertation (Uppsala, 1928), Zeits. f. Physik **93**, 450 (1933); J. M. Cork, Phys. Rev. **35**, 1456 (1930); J. H. Bearden, Phys. Rev. **37**, 1210 (1931).

[2] Allison and Armstrong, Phys. Rev. **26**, 701 (1925). See also Allison's excellent discussion in Compton and Allison, *X-Rays in Theory and Experiment*, page 698. For experimental support of the shallow penetration depths given by extinction formulae see recent work by W. Kossel and H. Voges, Ann. d. Physik **23**, 677 (1935).

compute, should be of the order of $1.2\times10^{-3}$ or 40,000 planes. Y. C. Tu[3] finds that calcite, rocksalt, KCl and diamond agree very well in giving the same value of $e$. Criticisms of the x-ray method of determining $e$ nevertheless have continued on the above grounds and it must be admitted that the superficial layers of a crystal constitute such a specialized part of its volume that every effort should be made to extend the x-ray measurements so as to make the latter as representative as possible of the entire volume whose density has been measured. Unless this is done there is certainly a logical hiatus in the above reasoning by which we arrive at the value of $e$ and it is the closing of this gap by a solid experimental procedure which we here chiefly wish to report.

(2) It is not out of place to mention that the methods we have employed also conclusively answer the criticism sometimes raised that the crystal may contain minute cracks, gaps or crevices in its structure.

(3) Another type of criticism which we have never heard raised but which we believe might have occurred to the truly critical minded is a question as to the precise validity of the Eq. (1) relating $\theta$, $\lambda$ and $d$, when the variables are regarded as having an absolute significance. A really critical defense of this equation requires an appeal to the dynamical theory of x-ray diffraction. Darwin, Ewald, Prins, and Laue have all contributed brilliantly to this subject. Nevertheless the dynamical theory for the space grating, taking account of mutual to and fro interaction between all of its parts, becomes so complicated that none of the treatments can quite be regarded as straightforward rigorous solutions of the wave equation for the case of a medium with a threefold periodic distribution of refractive index with the same beautiful generality and finality of the corresponding treatment by Eckart[4] on diffraction from ruled plane gratings. The effect of extinction about which there is yet very little good experimental information probably operates to produce very rapidly changing intensities and amplitudes of the electromagnetic radiation from point to point within the crystal. Such an assumption as the immediate reorganization of secondary dipole wavelets to form plane waves inside the crystal, so essential to Ewald's theory, or the assumption of constancy of phase displacement for all atoms might not be quite correct for instance. The precision measurements in the third order here described using calcite powdered to the order of $10^{-4}$ cm and smaller seems to us to answer completely any objections founded on doubts as to the rigor of the dynamical theory since the simple elementary theory of Laue or Bragg must certainly apply to crystals so small that the radiation is negligibly extinguished in passing through them.

## II. Search for the Most Conclusive Method

The idea of the powdered calcite method of answering the above objections only came to us as an evolution from two other methods which after much research we felt did not meet critical objections which we ourselves could raise. It is probably valuable therefore to describe as briefly as possible the pitfalls discovered in this way the better to emphasize what must be avoided if a truly reliable conclusion is to be drawn. Furthermore we ran across certain interesting new and as yet unexplained phenomena, well worth reporting for themselves, in this search for a conclusive method.

### Two crystal spectrometer studies

Our first attempt consisted in a comparison, by means of the two crystal spectrometer, of the calcite reflection angles for the two cases which we called briefly Bragg reflection and Laue reflection. We reasoned that in the Laue case with the incident beam entering one face and the reflected beam emerging from an opposite face after reflections by internal planes parallel to neither of these faces *the whole interior structure* of the crystal must have served for reflection of the radiation and the reflection angle should therefore be representative of the entire crystal just as was the mean density measurement. This method of course fails to meet criticisms (2) and (3) above however.

On account of the construction of the only two crystal spectrometer then available,[5] not the entire Bragg or Laue angle $\theta$ was measured but

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

[4] C. Eckart, Phys. Rev. **44**, 12 (1933).

[5] J. W. M. DuMond and A. Hoyt, Phys. Rev. **36**, 1702 (1930).

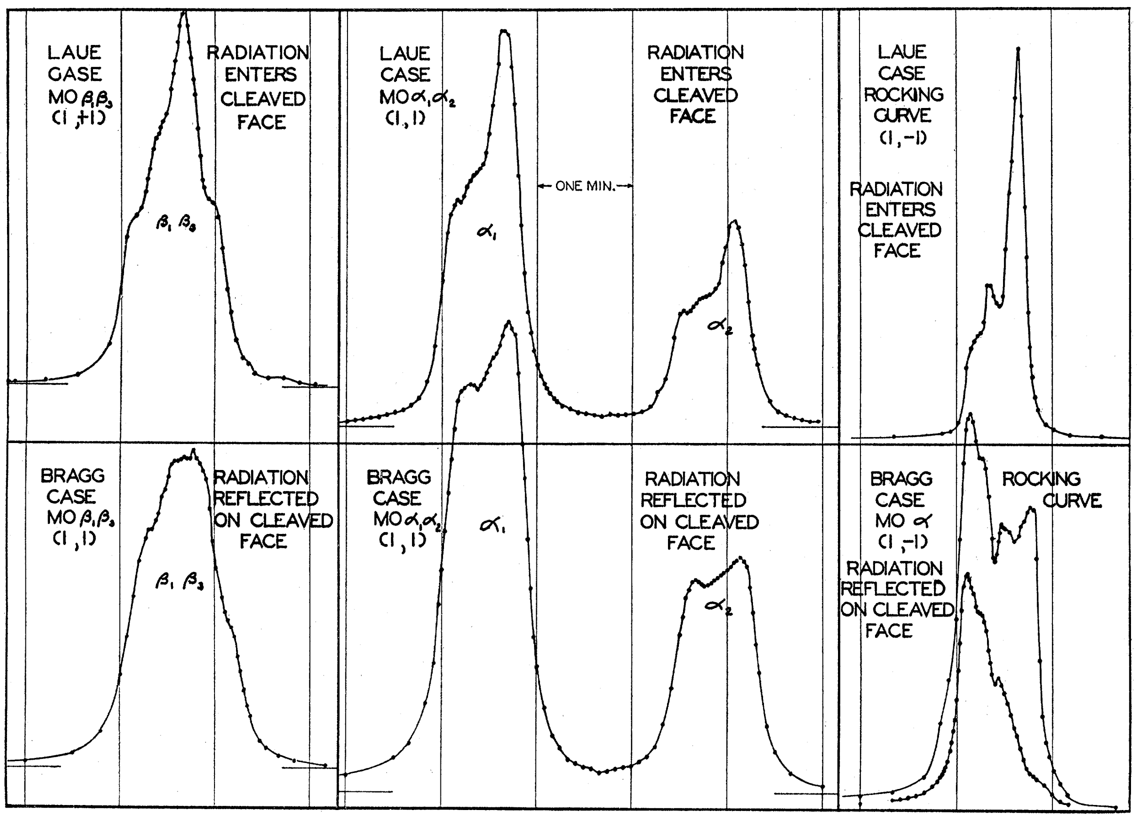

FIG. 1. Line structures obtained with etched calcite.

only the angular interval between two widely separated lines of the molybdenum $K$ spectrum. Crystal No. 1 of this spectrometer, a large and very perfect specimen of split calcite obtained from Steeg and Reuter in Hamburg was regarded as the collimator. Crystal No. 2 was very thin and could be oriented so as to reflect the collimated beam from No. 1 either in Bragg reflection from its large flat surface or in Laue reflection with the beam traversing its thin dimension reflected from internal planes parallel to a cleavage surface, in this case the thin edge of the flake. All appropriate alignments of the crystals by optical reflections from the faces and from the thin edge were carefully attended to. Gliding of the reflecting region across the crystal faces in the exploration of a spectrum was prevented by the mechanism of the spectrometer and x-ray table support. The effort was to see whether the angular interval between two given lines would be identically the same for the Bragg case as for the Laue. One of the first calcite samples used for test was rendered thin by etching down a rectangular portion in the center of a thicker (5 mm) slab with dilute HCl squirted through a fine nozzle. The etching did not proceed very uniformly and had to be controlled by stopping off various regions from time to time with wax. The thin window so formed varied in thickness from 0.5 to 0.2 mm. The unetched cleavage face on the reverse side could be used for Bragg reflection.

The etched crystal yielded the surprising line structures of Fig. 1. Prominent facts and inferences about these curves are: (1) The "lines" are about 3 times as broad as those usually observed with good calcite though the specimen was initially of the highest quality. (2) The curious rugged profile of each line, suggesting the presence of several simple component lines partially resolved, is reproduced for quite different wave-lengths (Mo $K\alpha_1$ Mo $K\beta_{1,\,3}$). (3) The invariability of pattern for *different* wave-lengths indicates that these component peaks are caused by a variety of orientations in the crystal rather than by a variety of grating constants. (4) A composite structure appears even in Bragg reflection for the unetched and apparently quite undamaged cleavage face on the opposite side to the etched surface. This may be caused either by released strains and disorientations of parts of the crystal where etching occurred extending themselves elastically through the thin dimension of the crystal to the unetched face or by the penetration of radiation from the unetched face through to the disturbed etched region sufficiently to permit considerable reflection there. (5) The rocking curves in the (1–1) order both in Bragg and Laue reflection also exhibit a composite broad structure but the structures in Laue and in Bragg reflection for (1,1) and (1–1) orders, four cases in all, have each a different characteristic profile.

These results which we cannot explain are the more surprising since it has recently been shown that the rocking and reflection curves can actually be markedly narrowed for calcite by appropriate light etching. This etched sample was obviously useless for our primary purpose. These results made us perhaps overcautious in regard to the possible existence of internal stresses in calcite which may have been released and thus rendered observable by the nonuniform etching process.

The work with the two crystal spectrometer was continued with thin cleaved plates of calcite for the crystal No. 2. Several good thin samples a millimeter or less in thickness were obtained. A great deal of experimentation was required to work out the best mounting for such thin and easily deformed flakes and much trouble was encountered with slight angular shiftings of the flake in its mount. In order to get reliable results which would average out any slight effect of curvature of the flake it was eventually found essential to take measurements of the angular interval between lines from both sides of the crystals both for the Bragg and Laue cases. Slight differences of temperature in different parts of the spectrometer, caused by a lamp used to read the angle scale, were found to cause some of the anomalies. Some mysterious erratic shiftings of the line positions with time were never completely explained but fortunately disappeared in our later and more careful work. Our first observation before all of these difficulties had been found and corrected happened to show by pure accident a difference between the angular intervals for Laue as compared to Bragg reflection indicating a difference in grating constant for these two cases of 0.2 percent and of the right direction to explain the, at that time, current magnitude of the discrepancy between x-ray and oil drop values of $e$. The possible importance of such a result made it imperative to check the two crystal spectrometer work by an independent method which would permit of measuring with precision the *entire* diffraction angle in Laue reflection. We therefore constructed an especial precision photographic spectrometer, to be described below, which yielded Laue diffraction angles with identically the same thin calcite crystal that had been used on the two crystal spectrometer in complete agreement with the most reliable determinations of Bragg diffraction angles to well within the estimated error of the method (one part in six thousand).

To eliminate all uncertainties we continued the two crystal spectrometer comparisons and found that with a sufficient number of precautions and especially that above mentioned of taking an average of the angular interval measurements from both faces of the crystal to eliminate minute curvature effects we could obtain complete and satisfactory agreement between the Bragg and Laue angular intervals. The slight shifting effect of differential absorption across the width of a line in Laue reflection was established as negligible. Lines $\alpha_2$ and $\beta_2$ of molybdenum were used. An aluminum filter was introduced in the case of the $\alpha_2$ line as a convenience to make the intensity comparable to that of the $\beta_2$ line

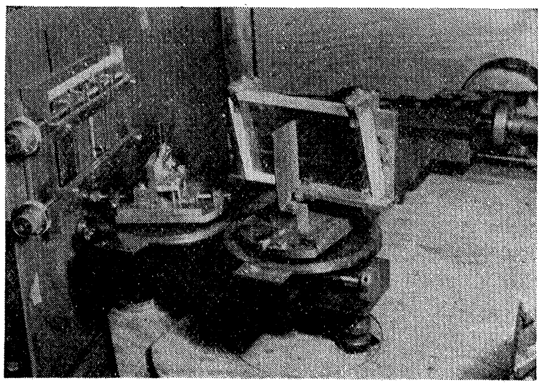

FIG. 2. Two crystal spectrometer arrangement for comparing Laue and Bragg diffraction angles.

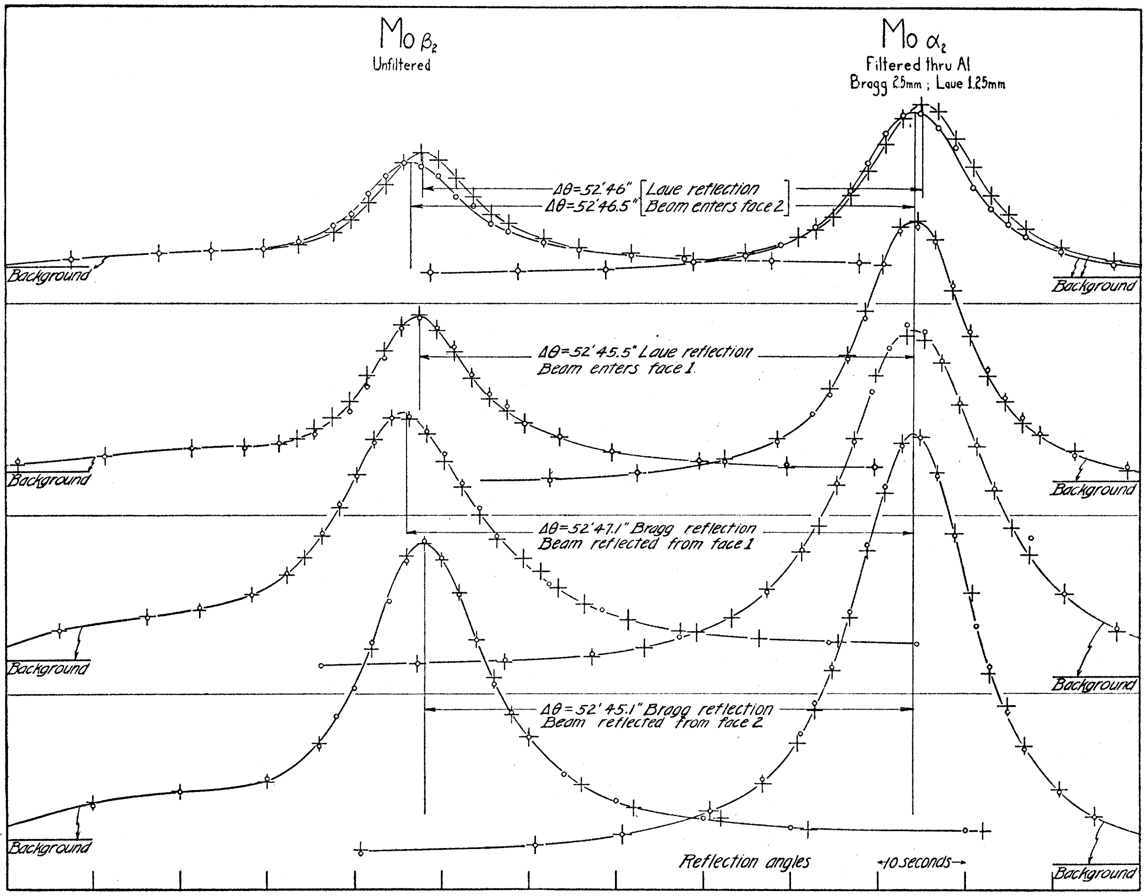

FIG. 3. Angular intervals between Mo $K\alpha_2$ and Mo $K\beta_2$ lines obtained on two crystal spectrometer comparing Laue and Bragg cases.

without changing the electrometer sensitivity. A thinner filter was appropriate for the Laue case than for the Bragg since the crystal itself is a strong filter. Fig. 2 shows the two crystals in place in the two crystal spectrometer while Fig. 3 shows the final results of the angular interval comparisons with this method.

In the Laue reflection work with the two crystal spectrometer it was found that the symmetry and width of the lines depended greatly on the region of the crystal used for reflection in the case of all samples. Regions too near the point of support were always "bad" but other regions with no such easily explained cause also showed distortions of line shape. Such distortions often seemed present at, as nearly as we could estimate, the same general regions in Bragg reflection. A suspicion could have appeared at this point that our Laue measurements were not as representative of the interior portions of the crystal as we at first thought. At this point however we merely felt the strong need for some statistical method which would free the x-ray measurements of the individual peculiarities of different crystals and of different regions in the same crystal.

## Study of Laue reflection with precision photographic transmission spectrometer

Fig. 4 is a photograph of the precision photographic transmission spectrometer. Its chief novelty is the crystal and slit mounting. The crystal and slit are held on small independently movable carriages sliding in ways on the top of a brass disk which turns on a well made conical pivot whose axis is accurately normal to the plane bed plate surface of the instrument. The plate holder is carefully made so as to maintain the photographic emulsion also accurately normal to the bed plate surface. By means of appropriate slides and leveling screws the slit was placed accurately parallel to and in coincidence with the axis of rotation of the pivot by reversals under a microscope with cross hairs and the thin crystal flake by means of other slides and leveling screws had its vertical thin edge and its flat face both made parallel to the pivot axis by optical reflections. One of the slides permitted moving the crystal flake so that one face stood very close indeed to the jaws of the slit. By further optical adjustments the pivoted disk was so oriented that a plane through the slit parallel to the reflecting planes to be used in the crystal flake would strike the photographic plate accurately normally and a small lead shield with a fine slit was placed at this point on the plateholder opening, just where the foot of this perpendicular fell on the plate, to serve as a fiducial mark. The pivot was firmly clamped during x-ray exposure. Initially, spectral line photographs were taken with the crystal on the x-ray tube side of the slit. By swinging the spectrograph with respect to the x-ray tube, $K\alpha$ lines of the Mo spectrum could be formed on the plate by Laue reflection both from the right and from the left side of the lattice planes inside the crystal flake, the transmitted beam being shielded in each case from fogging the plate by a movable lead slide. The fiducial center mark was also recorded on the plate by a short auxiliary exposure through the slit and crystal with direct radiation. In all cases the foot of the perpendicular from slit to plate proved to be so accurately centered between the right-hand and left-hand spectra that no correction for geometrical asymmetry would have been significant. The distance from slit to plate was carefully measured with a cathetometer and found to be 606.5±0.1 mm. The cathetometer scale was checked on the same comparator used for measuring line separations on the plate. Fig. 5 shows the geometry of the set-up.

Very beautiful and finely resolved lines of the $\alpha$ doublet were obtained on several plates. Compton's precise measurements[6] of the Bragg reflection angle in calcite with a precision Société Génevoise two crystal spectrometer yielded an angle of 6° 42′ 36″ for the $\alpha_1$ line of molybdenum. If this same angle holds for Laue reflection the separation $\delta$ of the right- and left-hand lines on our plate should be 142.710 mm. On two photographic exposures we obtained

$$\begin{array}{l}\delta_1=142.725\\ \delta_2=142.712\\ \hline \delta_m=142.719\text{ mm.}\end{array}$$

These Laue reflection data are in better agreement with Compton's Bragg data then the precision of our cathetometer measurement warranted. These cathetometer measurements, good to 1 part in 6000, constitute the determining element in the accuracy of this method and the agreement between Bragg and Laue reflection angles was thus established to that relative precision.

This was identically the same crystal flake used on the two crystal spectrometer and it was the above result that completely proved the unreality of the preliminary apparent discrepancy between Laue and Bragg angles obtained at first with the two crystal method.

As a further check we also made a measurement with the photographic transmission spectrometer using $(1\bar{1}0)$ planes (these indices are referred to cleavage axes). These planes are shown in Fig. 6 which is a projection of a unit cleavage cell looking along one of its edges. It is evident that

$$d_{100}/d_{1\bar{1}0}=2\cos\tfrac{1}{2}\alpha.$$

Bearden gives $\alpha=105°\ 3'\ 29''$. The wider separation of the right- and left-hand spectra in this case required moving the plateholder to a new position closer to the slit. The new slit to plate distance (482.55 mm±0.03) was determined

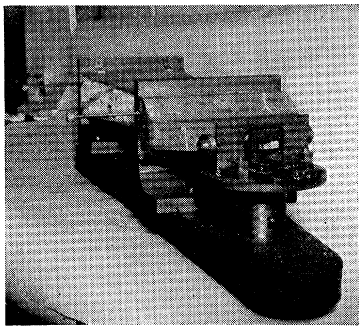

FIG. 4. Photograph of precision photographic transmission spectrometer. Slit and crystal are here in position of Fig. 7 or Fig. 9a.

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

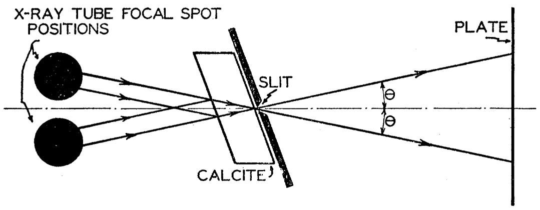

Fig. 5. Geometry of precision photographic transmission spectrometer as normally used for determining diffraction angles with slit on plate side of crystal. The radiation left the nearly horizontal target surface in the x-ray tube at a small glancing angle of about 5°. The diameter of the round focal spot furnished a sufficiently extended source just to permit the simultaneous reflection of the $\alpha$ and $\beta$ doublets with careful adjustment.

as before and the computed separation of the lines reflected from $(1\bar{1}0)$ based on Compton's Bragg (100) reflection data was $\delta = 138.613$ mm. On two plates we obtained

$$\begin{array}{c}\delta_1 = 138.621\\ \delta_2 = 138.614\\ \hline \delta_m = 138.617 \text{ mm.}\end{array}$$

This would furnish a complete check for this piece of calcite not only of the lattice parameter but of the angles characteristic of the calcite rhomb for reflection from internal planes were it not for the results of the next experiment.

### Laue reflection probably not a valid test of the interior of a crystal

As a last precaution we thought it would be safer to make quite sure that, in the above work with the two crystal spectrometer and the photographic spectrometer, the reflection was indeed coming from the interior of the crystal. To our astonishment and chagrin the contrary proved true.

We turned the crystal and slit mounting of the precision photographic transmission spectrometer round through 180° so that now the crystal was between the slit and the photographic plate. The geometry of the new arrangement appears in Fig. 7. Now instead of a fine line on the plate for each wave-length we expected to get a broad band of width $d_1$ and $d_2$ for the right- and left-hand spectra, respectively. The triangular region $OAB$ in the crystal we thought would be a field in which multiple to and fro selective reflection would take place so as to fill out the spaces between lines $A_1B_1$ and $A_2B_2$ with more or less uniform distributions of widths $d_1$ and $d_2$. Instead of this lines only appeared at $A_1$, $B_1$, $A_2$ and $B_2$ with negligible intensity between them. Fig. 8 shows an enlargment of a very short section of these doubled lines. For simplicity of discussion we will here describe the phenomenon entirely in terms of the appearance of a single monochromatic line, say $\alpha_1$.[7]

### Entry and exit surface Laue reflections not quite parallel

From the thickness of the crystal and the angle $\psi$ Fig. 7 we computed the separations $d_1$ and $d_2$ to be expected as 0.0232 cm and 0.0217 cm, respectively. The observed separations of the line pairs $A_1B_1$ and $A_2B_2$ turned out to be not quite equal to these expectations at all distances but to approach these values the closer the plate came to the crystal. The beams $A_1B_1A_2B_2$ which one would have expected to be propagated in parallel pairs turned out to have the members of each pair apparently very slightly convergent. This *might* have been an effect on the plate of the slightly increased overlapping of the members of a pair at greater distances as the breadths of the members increased slightly with increasing

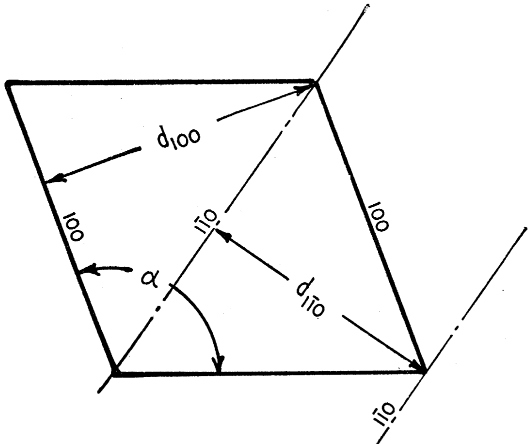

Fig. 6. Projection of unit cleavage cell of calcite looking along a direction parallel to one edge to illustrate the $(1\bar{1}0)$ planes in relation to the cleavage planes.

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[7] The effect of enhanced Laue reflection at a ground or otherwise disturbed crystal face is of course well known and understood. The crystals here used however had excellent cleavage surfaces with narrow rocking curves and we were quite unprepared for the almost complete absence of reflected intensity between $A$ and $B$.

distance. The tendency for doublet separations to appear smaller than they should as the members overlap more and more is a well-known illusion. We tend to doubt this explanation and to think the convergence real.

### Fluctuations of intensity along the lengths of the spectral lines

An even more surprising peculiarity of the spectral lines taken with the crystal in this position and one which we believe has never before been reported, is a more or less periodic fluctuation of the intensity vertically along the *length* of the line. Both these phenomena were observed in varying degrees in all the thin flake samples of calcite we examined, some of which had very marked fluctuations of intensity amounting to complete extinction of the line at roughly uniformly spaced intervals. A careful study of these fluctuations at different slit-plate distances with the x-ray tube at different vertical elevations with respect to the slit and plate convinced us that each of these fluctuations is definitely associated with some local condition permanently assignable to different localities in the crystal and is not as we thought at first some sort of Fresnel interference effect. It seems strange however that the extinguished points on the two lines forming a pair such as $A_1B_1$ seemed to occur at about the same vertical heights with more than accidental agreement. If, as appears probable, the two members of each pair are merely strongly enhanced reflections from the disturbed front and back surfaces of the crystal it is hard to see why these disturbances should be localized at corresponding points on the two sides of the thin flake. No such fluctuation of intensity along the length of the lines was observed with the slit between crystal and photographic plate.

### Faint radiation between the exit and entry Laue reflections

We had to settle the question as to whether the radiation was absent between the members of a pair such as $A_1B_1$ because of some sort of destructive Fresnel interference or whether its absence there was simply because the interior of the crystal failed to reflect. This we did by introducing auxiliary slit jaws $J_1$, $J_2$ with micrometer screw movements close behind the crystal as shown in Figs. 9a and 9b, so as to cut off at will either line $A_1$ or $B_1$ or both. It was found that with either member of the pair cut off the remaining member was unchanged. With both members cut off so as to have a slit that would only permit radiation $C_1C_1'$ or $C_2C_2'$ reflected from the interior of the crystal to reach the plate, some fifteen times as much exposure was necessary to obtain lines, and these lines were hazy, ill defined and unsuitable for precise measurement.

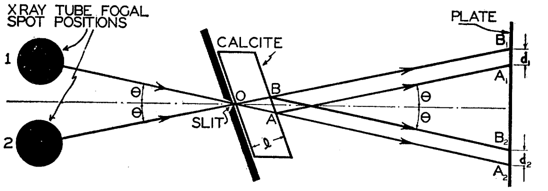

FIG. 7. Geometry of precision photographic transmission spectrometer as used to study entrance and exit surface Laue reflections. The slit is now on the opposite side of the crystal from the plate.

More work should certainly be done in the study of these strange effects for themselves but for the point at issue the methods so far described of studying Laue reflection in macroscopic calcite may be 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.

## III. THE POWDER METHOD A CONCLUSIVE ANSWER TO ALL THESE CRITICISMS

Since one is apparently restricted to investigations of a very superficial layer when using macroscopic calcite either in Laue or Bragg reflection *a conclusive answer to all these criticisms should come from a study of finely powdered calcite of grain size smaller than the extinction layer.* If one investigates the diffraction angles and density of crystals of size $10^{-4}$ cm on a side, so small that extinction is negligible in them, it is obvious that a statistical result truly representative of the entire sample is obtained both for density and diffraction. If it be a valid criticism that unbalanced forces near the surface of a macroscopic crystal render the density there somewhat dif-

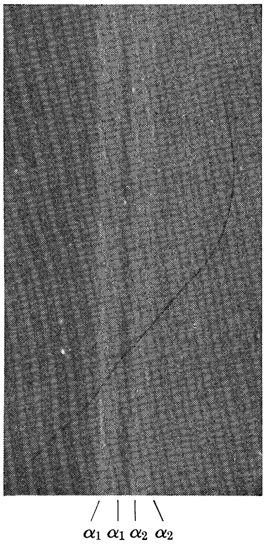

FIG. 8. Photographic reproduction of Laue reflections from exit and entry surfaces of a thin calcite crystal.

ferent from the mean then one might expect the density of the finely powdered calcite to be different from the mean density of macroscopic calcite. *It is important therefore to measure the density of the identical calcite powder used in the diffraction experiment.* This was done with a pycnometer with included thermometer.

### Pycnometric density determination on powdered calcite

The density of the pycnometer water was checked by weighing a known volume which had been measured out with a standardized "ausguss" pipette. The laboratory distilled water was 0.08 percent lower density than that given by the handbooks and it was necessary to redistill it in an all glass still and boil it to remove occluded gas. With these precautions the average deviation from the standard table values of six determinations of the density of this water was only three parts in one hundred thousand. The density of both macroscopic and microscopic calcite crystals was determined in the same pycnometer bottle as a check, the macroscopic samples being slivers as large as would go in the neck of the bottle. The macroscopic samples weighed 12 grams while the powdered samples ranged from 21 grams to 10 grams in amount. The powder was made by grinding in an agate mortar and rejecting the coarser grains by precipitation in water. The impalpable powder thus obtained had some visible grains under an immersion microscope of a size which we estimated as $2\times10^{-4}$ cm. The method of precipitation of course would give grain sizes ranging down below this upper limit into the submicroscopic. In measuring the diffraction rings from the powder the few isolated specks caused by reflection from the fortuitously oriented larger grains were ignored and the measurements were taken to the centers of the smoothly filled out parts of the rings only. It seems likely therefore that the grains actually involved in the measurements were very considerably smaller than these few largest ones seen in the microscope and that they constituted the bulk of the samples.

The results of our density determinations on macroscopic and powdered calcite are compared in Table I with the excellent data obtained by Bearden[8] on macroscopic calcite by weighing in fluids. The probable errors of our data are computed from internal consistency of the observations. The reproducibility of the measurements of the fine powder is indeed remarkable. In filling the pycnometer bottle containing the calcite powder 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 also helped.

It is easy to show that the solubility of calcite in water introduces an error of only one part in forty thousand in the density determination.

### The powder diffraction measurements

To obtain the maximum possible precision in the absolute determination of the size and shape of the lattice a Seeman-Bohlin spectrograph was used and reflections were chosen for such primary wave-length and Miller indices that the reflected beam would return almost directly backward to a region $FF'$ (see Fig. 10) not far from the pinhole

TABLE I. *Density of calcite.*

| STATE | METHOD | OBSERVER | DENSITY | PROBABLE ERROR | NO. OF OBSERVATIONS |
|---|---|---|---|---|---|
| Powdered | Pycnometer | Bollman | 2.71022 | +0.00035 | 6 |
| Macroscopic | Pycnometer | Bollman | 2.71085 | +0.00019 | 3 |
| Macroscopic | Immersion | Bearden | 2.71030 | +0.00003 | |

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[8] Bearden, Phys. Rev. **38**, 1389 (1931).

at $S$ through which the primary rays had entered. This means that $\theta$ in the equation $n\lambda = 2d \sin \theta$ is nearly 90°. Considering $\lambda$ as a known constant from grating wave-length determinations if we differentiate this equation and replace $\theta$ by $\alpha = \frac{1}{2}\pi - \theta$ (since the measurements of the diameters of diffraction rings centered around the entrance pinhole are nearly proportional to $\alpha$) we obtain

$$\alpha \tan \alpha(\Delta\alpha/\alpha) = \Delta d/d \qquad (3)$$

or for small $\alpha$ $\quad \Delta d/d = \alpha^2(\Delta\alpha/\alpha). \qquad (4)$

Thus if in radian measure $\alpha$ is of order 0.1 the relative error in determining the lattice constant $d$ is only one one-hundredth as great as the relative error committed in measuring on the film.

Nickel $K$ radiation was chosen for the work. A rather long wave-length is necessary in order to have reasonably intense reflections in calcite at angles $\theta$ near 90°. On the other hand too long a wave-length limits the depth of penetration by extinction whereas the whole point of the experiment is to have the penetration into the small particles as great as possible. In fact the two requirements, low extinction and strong reflection, are more or less mutually contradictory. The obvious solution is to tolerate the *weakest possible diffraction ring intensities that will yield acceptable precision in measuring their locations in order to get as little extinction as possible in the passage of radiation through the particles.* The reason for choosing nickel for the target was because we computed that the Ni $K\alpha$ lines would be just reflected in the third order from the $(1\bar{1}0)$ planes (cleavage system) of Fig. 6 at an angle $\theta$ slightly less than 90°. Measurements eventually were discarded on this reflection as it was found to be too faint and diffuse on account of the enormous dispersion at this large angle but three planes with other Miller indices were found to yield all the information needed from the nickel radiation. The target of the tube was made by nickel plating an old water-cooled copper target. A cylindrical Nonex glass envelope about $1\frac{1}{2}$ inches in diameter provided with a thin concave glass window in the end of a short side tube was blown around the cathode and target and a thoroughly outgassed charcoal trap in a side tube was kept in liquid air during operation.

The spectrograph had a lead alloy lining to reduce the general scattering. Diffraction exposures taken without the calcite powder but with the x-rays simply incident on the lead showed strong diffraction rings inconveniently located close to the calculated positions of diffraction rings from calcite. These were completely eliminated by covering the lead in the radiated area with several sheets of gold foil which in a test exposure showed no rings whatever in the region where our calcite rings appeared. The spectrograph had a tight cover provided with a gasket and could be evacuated with a fore pump. This precaution we found necessary to reduce the fogging and general background of the film. Even so the calcite diffraction rings were very faint and are unfortunately unsuitable for reproduction by half-tone process.

Fig. 11 shows the x-ray tube and the spectrograph with cover removed. The calcite powder which was made to adhere to the cylindrical

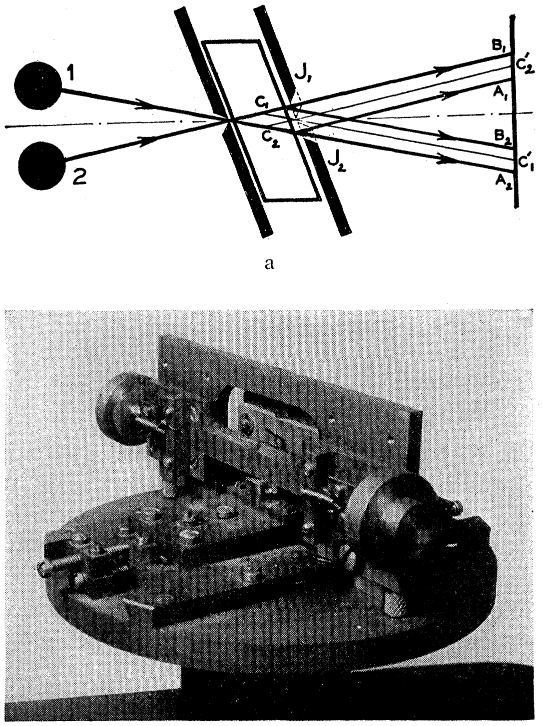

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FIG. 9a. Auxiliary slit jaws used in study of entrance and exit surface Laue reflections. 9b. Photograph of transmission spectrometer slit and crystal mounting with auxiliary jaws.

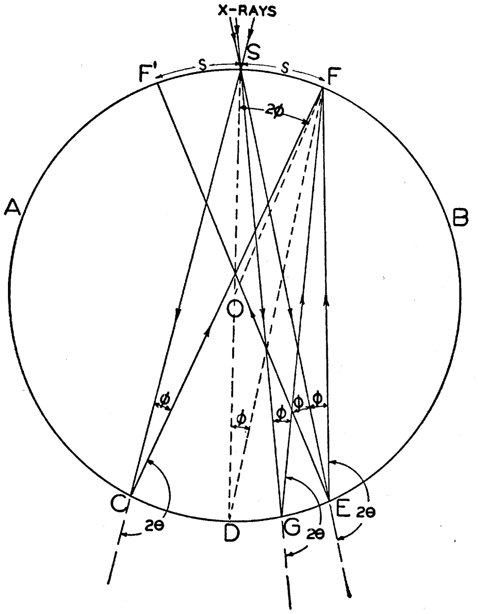

FIG. 10. Geometry of Seeman-Bohlin spectrograph.

surface with a tiny quantity of collodion can be seen as a white patch on the inner wall of the spectrograph. Part of the film holder and the slit both on the opposite side of the spectrograph can also be seen. The calcite powder sample had a thickness of 0.25 mm to correspond with the thickness of the double-coated x-ray film. The diameter of the spectrograph $D=6.905$ inches was carefully calipered inside at a number of points. The greatest deviation from uniformity of $D$ was one part in 7000.

## Identification of powder diffraction rings with Miller indices

It is of course absolutely essential to identify beyond all doubt the Miller indices corresponding to all powder rings measured. If a reciprocal lattice for calcite is constructed the coordinates of each point of which correspond to the Miller indices of a set of planes and a sphere is struck out centered at the origin with radius $R=(2\sin\theta)/\lambda$ Ewald has shown that any points of the reciprocal lattice lying on this sphere will correspond to the Miller indices of planes which can reflect radiation $\lambda$ under angle $\theta$. Two such reciprocal lattices were graphically constructed. The points lie in planes equally spaced in a vertical direction. In each plane the points lie at the corners of lozenge shaped cells having angles of 60° and 120°. Fig. 12 shows a projection of the reciprocal lattices looking along the vertical axis. A sphere of radius $R=(2\sin\theta)/\lambda$ was struck out in one of these for $\theta=75°\ 24'$ and in the other for $\theta=83°\ 39'$. This sphere intersects the equally spaced horizontal planes in circles as shown in the figure. Thus if a circle passes through a lattice point in the projection that point *may* correspond to a possible reflection. The method of constructing the reciprocal lattice by starting for convenience with the calcite lattice *in the hexagonal system* gives *all* possible calcite Miller indices and some which are *not* a part of the calcite system. These can be easily discarded since they do not yield integers for the Miller indices in the rhombohedral system. This method is thus a *completely exhaustive one* for enumerating the Miller indices of all calcite planes which can be responsible for reflections of $\lambda$ at the angle $\theta$. The following formula[9] gives the grating space $d_{h_1h_2h_3}$ for any set of Miller indices expressed in the rhombohedral crystallographic (not cleavage) system

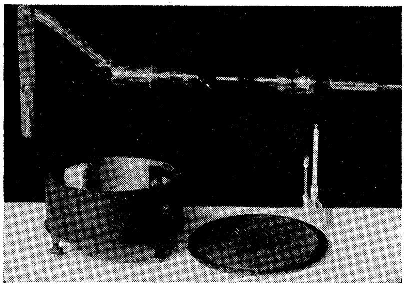

FIG. 11. Nickel target x-ray tube, Seeman-Bohlin spectrograph and pycnometer bottle.

$$d_{h_1h_2h_3}=\frac{a(1+2\cos^2\gamma-3\cos^3\gamma)^{\frac{1}{2}}}{[(h_1^2+h_2^2+h_3^2)\sin^2\gamma+2(h_1h_2+h_1h_3+h_2h_3)(\cos^2\gamma-\cos\gamma)]^{\frac{1}{2}}},\tag{5}$$

---

[9] For the structure of calcite and its representation in different systems of reference see Ewald-Hermann, *Structurbericht*, p. 292.

TABLE II. *Designation of all possible planes that have values of d appropriate to the regions in which powder rings were observed.*

| HEX. INDICES, $(H_1H_2H_c)$ | RHOMB. INDICES, $(h_1h_2h_3)$ | GRATING SPACE, $d_{h_1h_2h_3}$ | WEIGHT FACTOR, $P$ | STRUCTURE FACTOR, $F$ | INTENSITY | DEPTH OF PENETRATION TO ½ INTENSITY (cm) |
|---|---|---|---|---|---|---|
| 1,2,17 | 476 | 0.8532 | 12 | 3.66 | 161 | |
| 3,1,14 | 374 | .8528 | 12 | 4.38 | 230 | |
| 3,2,10 | 163 | .8557 | 12 | 8.04 | 774 | $0.585\times10^{-3}$ |
| 0,5,4 | $\bar{2}33$ | .8458 | 6 | 11.3 | 762 | $0.416\times10^{-3}$ |
| 5,0,2 | $\bar{1}4\bar{1}$ | .8586 | 6 | 4.38 | 115 | |
| $5,0,\bar{1}$ | $\bar{2}3\bar{2}$ | .8619 | 6 | 1.83 | 20 | |
| 0,1,20 | 677 | .8349 | 6 | 11.3 | 762 | $0.416\times10^{-3}$ |
| 2,4,15 | 357 | .8389 | 12 | 0 | 0 | |
| $0,4,\overline{13}$ | 733 | .8326 | 6 | 0 | 0 | |
| 2,5,11 | 146 | .8338 | 12 | 3.66 | 161 | |
| $\bar{5},5,5$ | 005 | .8366 | 6 | 0 | 0 | |
| 3,3,0 | $\bar{3}30$ | .8304 | 6 | 7.58 | 343 | $0.62\ \times10^{-3}$ |

in which to an accuracy sufficient for the identification of diffraction rings the constants can be assumed to have the value $a=6.361$A, $\gamma=46°\ 7'$.

A knowledge of the relative intensities to be expected from the various planes served as a final identification test. These were computed from the formula

$$I=KPF^2, \tag{6}$$

in which $K$ is simply a proportionality constant, $P$ is the permutation factor entering because some planes admit of reflection with the crystalline particle in more orientations than do other planes, and $F$ is the crystal structure factor. In computing the crystal structure factor, values of the atomic structure factors for Ca, C, and O were obtained from the work of Pauling and Sherman.[10] Table II gives all of the possible planes expressed both in hexagonal and rhombohedral crystallographic indices that have values of $d$ appropriate to the regions in which powder rings were observed. Referring to the rhombohedral indices the computed intensities immediately identify (163) and ($\bar{2}33$) as the planes giving the two observed reflections in the region 75° 24′ while in a similar way (677) was identified with the reflection in the 83° 39′ region. As before stated the reflection ($\bar{3}30$) which we have referred to in Fig. 6 did not present sufficient intensity and contrast to be used with certainty.

## Depths of penetration into the crystal particles

The depths of penetration to ½ intensity in Table II were computed from the formula for the extinction coefficient $\mu_e$

$$\mu_e=4\pi F\delta/Z\lambda\ \sin\theta_0, \tag{7}$$

in which $Z$ is the number of electrons in the calcite unit cell, $\delta=10^{-5}$ is the difference between the refractive index and unity for the wavelength $\lambda=1.658$A, $\theta_0=90°$ approximately. Note that the largest crystals observed with the microscope in our powder sample have dimensions only half the shallowest half penetration depth computed above. Thus in the worst cases the beam only lost about a quarter of its original intensity in passing through a single crystalline particle.

## Measurements of diffraction angles

Five different exposures were taken but since not all of these showed the same degree of contrast some of the lines could not be measured with certainty on certain of the exposures. Table III giving the observed distances $2s$ (Fig. 10) measured on the film indicates the

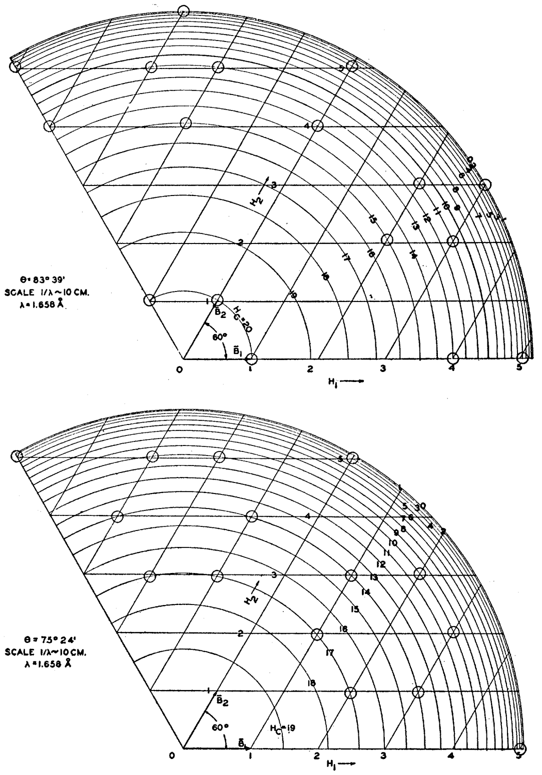

FIG. 12. Projection of calcite reciprocal lattice and circular intersections of propagation sphere with the lattice planes for two radii.

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[10] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

TABLE III. *Observed values of the distance 2s measured on the film.*

| MILLER INDEX | SPECTRAL LINE | FILM NO. 1 | 2 | 3 | 4 | 5 | MEAN |
|---|---|---|---|---|---|---|---|
|  |  | DISTANCES 2s (INCHES) |  |  |  |  |  |
| $h_1h_2h_3$ (1 6 3) | $\alpha_1$ | 7.05 | 7.07 | 7.06 | 7.05 | 7.05 | 7.056 |
|  | $\alpha_2$ | 6.79 | 6.75 | 6.75 | 6.80 | 6.75 | 6.768 |
| ($\bar{2}$ 3 3) | $\alpha_1$ |  | 5.70 |  |  | 5.67 | 5.685 |
|  | $\alpha_2$ |  | 5.39 |  |  | 5.30 | 5.345 |
| (6 7 7) | $\alpha_1$ | 3.78 | 3.79 | 3.80 | 3.75 | 3.76 | 3.776 |
|  | $\alpha_2$ | 3.30 | 3.30 | 3.26 | 3.29 | 3.30 | 3.290 |

inner consistency here. The resulting probable relative error in $d$ is of course far smaller.

Now by means of the formula

$$d=\lambda/(2\cos 2s/4D), \tag{8}$$

which can be easily shown to follow from the geometry of the spectrograph and assuming the wave-length values for Ni $K\alpha_1$ and $K\alpha_2$ as measured by Erikson[11] based on Siegbahn's conventional value of the calcite lattice constant

$$d_{100}=3.02904\text{A at }18°\text{C for calcite,}$$

$$\lambda_{\alpha_1}=1.65450,\quad \lambda_{\alpha_2}=1.65835,$$

we can compute the lattice constants of our planes in terms of the Siegbahn conventional scale. These are given in Table IV.

TABLE IV. *Lattice constants of planes in terms of Siegbahn conventional scale.*

| Indices Crystallograph Rhomb. $h_1h_2h_3$ | Angstroms $d$ From $\alpha_1$ | $d$ From $\alpha_2$ | $d$ average | Indices Cleavage Cell $c_1c_2c_3$ |
|---|---|---|---|---|
| 1 6 3 | 0.85500 | 0.85472 | 0.85486 | $\bar{6}$,14,2 |
| $\bar{2}$ 3 3 | .84510 | .84494 | .84502 | $\overline{12}$,8,8 |
| 6 7 7 | .83504 | .83510 | .83507 | 4,8,8 |

Cohen[12] has analyzed the sources of error in precision work with the Seeman-Bohlin spectrograph. Using his formula and also taking into account the inner consistency of the measurements on 2$s$ we estimate *very conservatively* that the total error from both systematic and random causes cannot exceed 0.05 of one percent in the above results of Table IV. The agreement between the results on $\alpha_1$ and $\alpha_2$ is in accord with this estimate.

### Determinations of the angle β of the calcite cleavage cell

The above data are all that we need to determine the angle $\beta$ characteristic of the calcite cleavage cell. This is the angle which enters into the function $\Phi(\beta)$ in the formula (2) by which $e$ is computed. If $c_1c_2$ and $c_3$ are the Miller indices in terms of the cleavage cell we have

$$d_{c_1c_2c_3}=\frac{c(1+2\cos^3\beta-3\cos^2\beta)^{\frac{1}{2}}}{[(c_1^2+c_2^2+c_3^2)\sin^2\beta+2(c_1c_2+c_2c_3+c_1c_3)(\cos^2\beta-\cos\beta)]^{\frac{1}{2}}}. \tag{9}$$

The ratio of the $d$'s for any two different sets of planes is then sufficient to calculate $\beta$. If the subscripts $i$ and $k$ refer for brevity to two such different sets of planes we have

$$\cos\beta=\frac{\{n_k-n_ib_{ik}^2\}\mp\{[n_k-n_ib_{ik}^2]^2+4[a_ib_{ik}^2-a_k][m_k-m_ib_{ik}^2]\}^{\frac{1}{2}}}{2[a_k-a_ib_{ik}^2]}, \tag{10}$$

where $b_{ik}=d_i/d_k,\quad m=c_1^2+c_2^2+c_3^2,\quad n=2(c_1c_2+c_1c_3+c_2c_3),\quad a_k=n_k-m_k,\quad n_i-m_i=a_i.$

The three sets of planes observed in our powder camera thus permitted three ratios $b_{ik}$ to be formed from which three independent determinations of $\beta$ were computed as follows

| Pairs of Cleavage cell indices | Values of $\beta$ | Mean value of $\beta$ |
|---|---|---|
| (4,8,8)/($\overline{12}$,8,8) | 101° 53′ 40″ | 101° 54′ 18″±48″ (Probable error from inner consistency) |
| (4,8,8)/($\bar{6}$,14,2) | 101° 52′ 51″ |  |
| ($\overline{12}$,8,8)/($\bar{6}$,14,2) | 101° 56′ 24″ |  |

This should be compared with Bearden's value of $\beta$ for macroscopic calcite[13]

$$\beta=101°\ 54'\ 4''\pm10''.$$

### Determination of d for the cleavage planes in microscopic calcite

We are now in a position to compute the value of $d$ for the cleavage planes in our microscopic

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[11] Eriksson, Zeits. f. Physik **48**, 360 (1928).

[12] M. U. Cohen, Rev. Sci. Inst. **6**, 68 (1935).

[13] Bearden, Phys. Rev. **38**, 2089 (1931).

calcite for comparison with macroscopic values. We proceed by first computing the lattice parameter $C$ of the cleavage cell by means of the formula

$$C_i = d_i \frac{(m_i \sin^2\beta + n_i(\cos^2\beta - \cos\beta))^{\frac{1}{2}}}{(1+2\cos^3\beta - 3\cos^2\beta)^{\frac{1}{2}}}; \qquad i=2,3,4 \quad \beta = 101^\circ\, 54'\, 18'' \tag{11}$$

Three different values distinguished by subscript $i$ were obtained from the data for the three different sets of planes observed with the result

$$C_2 = 12.8238\text{A}, \quad C_3 = 12.8194\text{A}, \quad C_4 = 12.8159\text{A},$$

all of course on the Siegbahn scale. The mean value is

$$C = 12.8197 \pm 0.0016\text{A (Siegbahn scale)}$$
$$\beta = 101^\circ\ 54'\ 18'' \pm 48''.$$

Remembering that the cleavage $d_{100}$ is really $d_{400}$ in the 32 molecule cell we have

$$\begin{aligned} d_{400} &= \frac{12.8197(1+2\cos^3\beta - 3\cos^2\beta)^{\frac{1}{2}}}{(16\sin^2\beta)^{\frac{1}{2}}} \\ &= 3.02823\text{A on the Siegbahn scale.} \end{aligned} \tag{12}$$

The corresponding value for macroscopic calcite *on the same scale is* $d_{400} = 3.02904$A.

### Value of electronic charge from grating wave-length data

Transformation from the Siegbahn scale to the absolute scale of lengths as determined by ruled gratings was effected by a comparison of the crystal results of Wennerlöf[14] on Cu $K\alpha_1$ radiation $\lambda_{\alpha 1} = 1.537395$ (Siegbahn scale) with Bearden's measurement of the same wave-length with a ruled grating $\lambda_g = 1.5406 \times 10^{-8}$ cm. Using then the value of $d$ on the absolute scale together with $M = 100.078 \pm 0.005$, $Q = 2.89270 \pm 0.00021 \times 10^{14}$ abs. e.s.u., $\rho = 2.71022 \pm 0.00035$ g/cc, $\Phi(\beta) = 1.09602 \pm 0.00048$ one obtains by formula 2

$$e = 4.799 \pm 0.007.$$

## IV. Conclusions

The results of this investigation we believe conclusively and permanently answer all three of the objections raised to the x-ray crystal method of determining $e$. The angles of diffraction are representative of the entire powder sample since the half depth of penetration computed from the extinction coefficient is double the dimensions of the largest crystals used in the sample. The density determination therefore applies to identically the same calcite as has been used to diffract the x-rays.

The agreement between the densities of microscopic calcite and macroscopic calcite as well as the agreement of absolute size and shape of the lattice cell for these two is surprising evidence of the permanence of the lattice structure against mechanical maltreatment by powdering.

The elementary diffraction theory of Laue or Bragg must apply to the case of diffraction by crystals so small that the radiation is negligibly extinguished in passing through them and hence any critical objection to the crystal determination of $e$ based on doubts as to the absolute rigor of the dynamical theory of x-ray reflection are invalidated by our results.

## V. Acknowledgments

Dr. V. A. Brown (University of Arizona) did a part of the work falling under the heading of "Search for a Conclusive Test" as his Thesis for the Doctor's degree and we wish here to express our sincere appreciation for his assistance. Our sincerest gratitude also goes to Dr. J. H. Sturdivant of this Institute for his helpful discussions and suggestions regarding the analysis of the powder diffraction data.

The funds for this investigation are derived from the gift of Dr. Leon L. Watters of New York City for research work in x-rays and atomic structure known as the Watters Memorial Research Fund given by Dr. Watters as a memorial to his wife, Frances Hayes Watters. We are grateful for this opportunity to express our deep appreciation of his gift.

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[14] Wennerlöf, Ark. Met. Astr. O. Fys. (A) **22**, No. 8 (1930).

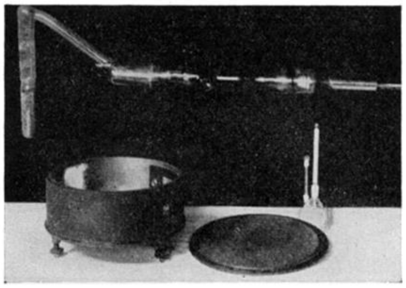


FIG. 11. Nickel target x-ray tube, Seeman-Bohlin spectrograph and pycnometer bottle.

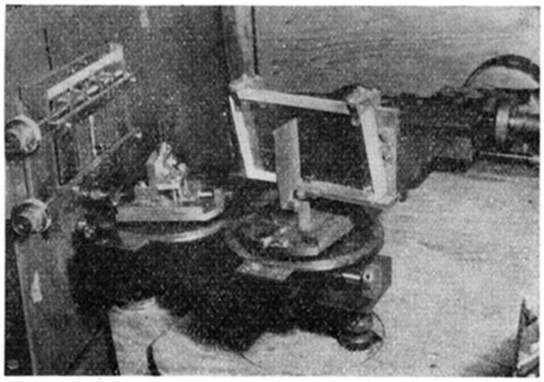


FIG. 2. Two crystal spectrometer arrangement for comparing Laue and Bragg diffraction angles.

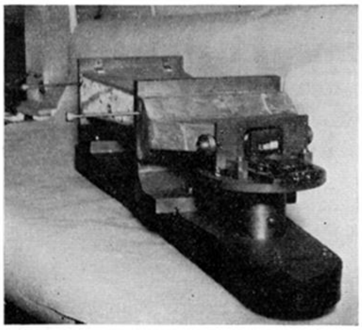


FIG. 4. Photograph of precision photographic transmission spectrometer. Slit and crystal are here in position of Fig. 7 or Fig. 9a.

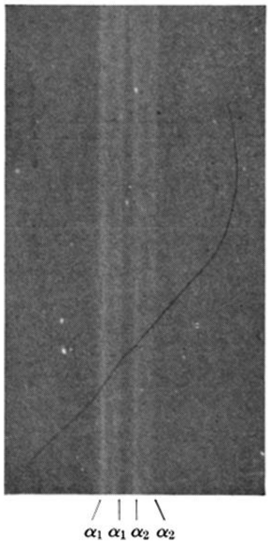
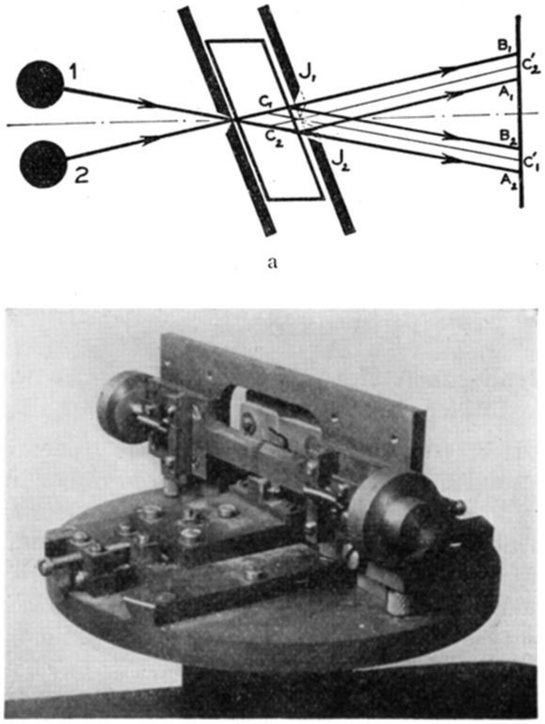


FIG. 8. Photographic reproduction of Laue reflections from exit and entry surfaces of a thin calcite crystal.



a

b

FIG. 9a. Auxiliary slit jaws used in study of entrance and exit surface Laue reflections. 9b. Photograph of transmission spectrometer slit and crystal mounting with auxiliary jaws.