THE USE OF THE OSCILLATION METHOD IN DETERMINING THE STRUCTURE OF ANALCITE

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INTRODUCTION

The optical anomalies of analcite, $NaAlSi_2O_6 \cdot H_2O$[1] have led mineralogists to suspect that analcite is not cubic but pseudo-cubic. X-ray investigations by the writer[2] have failed to furnish any clue as to its pseudo-structure, however. Analcite, therefore, may be regarded, for the present, as cubic holohedral. The forms (211) and (100) are well developed, as a rule, especially on crystals from the Cyclopean Islands which were used in this investigation. The oscillation spectrograms were made with the apparatus of Schiebold and Rinne.[3] For an understanding of the symbols and the terminology used in this paper it is essential that the reader refer to the paper "The oscillation method of X-ray analysis of crystals."[4] The references to it will be followed by "*Op. cit.*" in the text in order to avoid too many footnotes. The writer is greatly indebted to Prof. E. Schiebold and Prof. F. Rinne of the University of Leipzig, Germany, for the interest and help given to the author in this investigation.

The first step in the determination of a structure of a mineral is the measuring of the lengths of the edges of the unit cell and the finding of the fundamental Bravais lattice. Three of the fourteen Bravais lattices, the simple cube, the face-centered, and the body-centered cube, belong in the cubic system.

In the simple cube the three cube edges are the elementary primitive translations, that is the shortest vectors or *directed* distances from an atomic center to exactly identical atomic centers. The three elementary primitive translations in the face-centered cube are the three face-diagonal directions from one of the corner atoms. On them identical atomic centers are encountered at a distance of $\sqrt{2}/2 \cdot a_0$, a_0 being the length of the edge of the unit cube. The three elementary primitive translations in the

[1] Hintze, C., HANDBUCH DER MINERALOGIE, vol. **2**, 1897, p. 1712. Doelter's HANDBUCH DER MINERALCHEMIE, vol. 2, 2. Hälfte, 1917, p. 350.

[2] Die Struktur des Analcims: I. Die Raumgruppe, *Zeit. f. Krist.*, in press.

[3] See Figs. 4a and 4b, Schiebold, E., Die Drehkristallmethode, *Fortschritte der Min., Krist. und Petrographie*, vol. **XI**, 1927, pp. 125–126.

[4] Gruner, John W.; *Am. Mineral.*, vol. **13**, 1928, pp. 123–141.

body-centered cube are two edges a_0 and half the body diagonal which is $\sqrt{3}/2 \cdot a_0$ in length.[5]

It is obvious now that we can place a cubic crystal in its correct fundamental lattice, if we can measure the primitive translations in the directions of the cube edge [001], the cube face diagonal [110] and the body diagonal [111]. This can be done easily with the oscillation method. Three spectrograms of the crystal are necessary. Each one is a record of the crystal oscillated about one of the three directions given above.

Oscillation about the Edge of the Cube [001].

A good cube face of analcite is selected and mounted in the crystal holder (which may be similar to those on goniometers) in such a manner that the face is in a plane with the axis of oscillation and with the incident ray at the starting position. By "starting position" is meant the position of the crystal holder when the oscillating movement is reversed and the incident ray just parallels the crystal face. The face of the cube is turned in its plane till an edge [001] is parallel to the axis of oscillation. In order to get sharp-edged reflections on the photographic plate the Seemann wedge method is used. It consists in lowering a wedge of platinum or tungsten within 0.1 to 0.2 mm. of the crystal face in such a manner that the edge of the wedge lies exactly in the axis of oscillation.[6] This method insures a sharp edge on the side of the spot away from the axis of oscillation. The oscillation gear is set in motion after it is adjusted to turn 30° about the axis and then come back to the starting position. This motion is repeated at the rate of one oscillation in about 15 to 30 minutes. Monochromatic radiation from a molybdenum Coolidge tube was used for about two hours at 50 to 60 kilo volts and 5 to 6 milliamperes.

On the developed plate the middle of the sharp edge of each reflection is marked with India ink, by means of a dot and a number. The polar coordinates of each dot are recorded $\bar{\phi}$ in degrees and $\bar{r}$ in millimeters (*op. cit.* p. 127). The recording can be done best with a magnifying cyclometer. From the values $\bar{r}_{hkl}$ and

[5] Bragg, W. H., and Bragg, W. L.; X-rays and Crystal Structure, *London*, 1925, p. 78.
Wyckoff, R. W. G., The Structure of Crystals, *New York*, 1924, p. 56.

[6] Schiebold, E.; *op. cit.*, p. 140.
Wyckoff, R. W. G.; *op. cit.*, p. 166.

$\bar{\phi}_{hkl}$ of each spot the polar coordinates $R_0 \cdot \sin \alpha_{hkl}$ and $\rho_{p_{hkl}}$ of each point in the corresponding reciprocal lattice are calculated as follows.

Dividing $\bar{r}$ by r, the known distance from the axis of rotation to the photographic plate, the glancing angle α is obtained.

$$\frac{\bar{r}}{r} = \tan 2\alpha \qquad \text{Equation (3) } op.\ cit.$$

With α and $\bar{\phi}$ the angle ρ_p is found.

$$\cos \rho_P = \cos \alpha \cdot \cos \bar{\phi} \qquad \text{Equation (7) } op.\ cit.$$

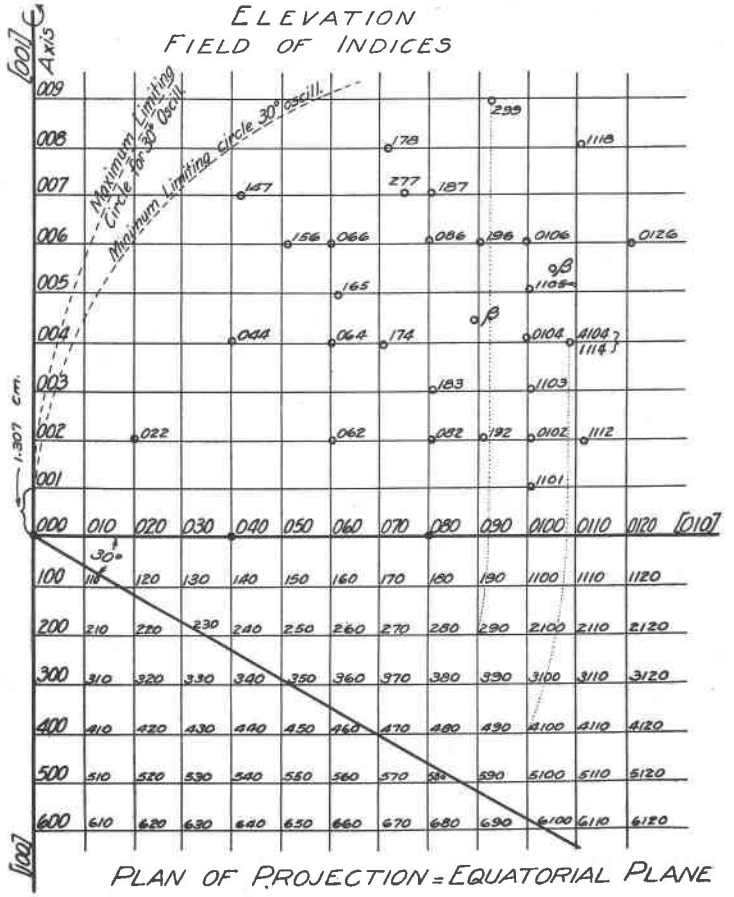

Figure 1.

$R_0 \cdot \sin \alpha$, the other coordinate is obtained by multiplying sin α by R_0, a constant. $R_0 = 500$ mm. The values for each sin α and ρ_p are given in the sixth and eighth columns of Table I. With these coordinates the points are plotted. The axis of rotation [001] is made the ordinate. The abscissa normal to the axis is the direction [010]. This is shown in the elevation of Fig. 1. Only the upper half of it is reproduced because the half on the photographic plate below [010] is symmetrical with respect to the upper one. (See for example Fig. 4). In Table I, however, all of the points of both halves are recorded. The plan below [010] in Fig. 1 is to be imagined as lying in the equatorial plane of the sphere of reflection at right angles to the axis of oscillation. The incident ray is parallel [100] at the starting position. Since an understanding of these directions is very important let a case in the orthorhombic system be considered, for illustration. Let the plane $a = (100)$ be taken. The directions [010] and [001] lie in it. These are the b and c axes, respectively. If we adjust the plane so that the direction [010] is parallel to the axis of oscillation and the plane is also parallel to the incident ray at the starting position, the direction [001] automatically has been made parallel to the incident ray at the starting position. The normal to the directions [001] and [010] obviously is the a axis or the direction [100]. In the reciprocal lattice the primitive translation a' (*op. cit.*, p. 129) is laid off in this direction [100] which is the abscissa in the projection. In other words that direction in the right-angled systems is the abscissa which is normal to the adjusted plane containing the axis of rotation and the incident ray at the starting position.

Returning to the case of analcite, the projection of the reciprocal lattice Fig. 1 reveals that the plotted points lie on parallel lines normal to the direction of the axis. They are the layer lines of I kind (*op. cit.*, p. 134) and equidistant from one another. This distance is $1/T_{001}$ (*op. cit.* Fig. 11), or we might say that it is the length h_{001} of the vector $\mathfrak{h}_{001}$ (the distance from 0 to point 001). But by equations (12) and (13) *op. cit.*

$$h_{001} = \frac{R_0 \lambda}{2d_{001}} \tag{18}$$

Substituting for h_{001} the average measured distance 1.307 cm. between layer lines of I kind, for R_0 500 mm., for λ $0.70759 \cdot 10^{-8}$

cm. $= k\alpha$ radiation of the molybdenum target, and solving for d_{001} we get

$$d_{001} = \frac{50\text{cm} \cdot 0.70759 \cdot 10^{-8}\text{cm}}{2 \cdot 1.307\text{cm}} = 13.54\text{Å}$$

The length of the edge of the cube is 13.54 Å. This value is probably correct within 2 to 3 per cent.

The reflections in the projection are also arranged in lines parallel to the direction [001]. These are the layer lines of *II* kind. Since [001] and [010] are equivalent in the cubic system the distance 1.307 cm. is also laid off along [010] and lines parallel to the axis are drawn through these points. The resulting lattice of squares can be supplied with indices as shown. It will be noticed that many reflections lie at intersections. For these the indices may be read off directly by counting the lines in the directions [010] and [001]. The indices must satisfy the equation:

$$s = hu + kv + lw = 0, \pm 1, \pm 2, \pm \text{integer} \quad (op.\ cit., \text{p. } 138) \qquad (19)$$

in which s is the index of summation, that is the number of the layer lines of *I* kind and $[uvw]$ the axis of oscillation, in our case [001]. Therefore the equation is simplified to:

$$s = l = 0, \pm 1, \pm 2, \pm \text{integer}$$

The two equations for the layer lines of *II* kind are: (*op. cit.*, p. 140)

$$h' = hu_1 + kv_1 + lw_1 = \text{constant} \qquad (20)$$

$$k' = hu_2 + kv_2 + lw_2 = \text{constant} \qquad (21)$$

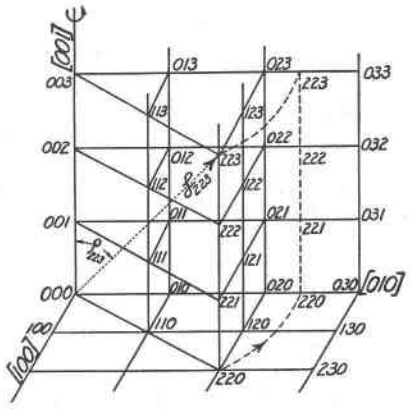

Figure 2.

Since $[u_1v_1w_1]$ and $[u_2v_2w_2]$ coincide with the crystallographic axes $a=[100]$ and $b=[010]$, respectively, these equations become:

$$h'=h=\text{constant along each layer line,}$$
$$k'=k=\text{constant along each layer line.}$$

All three equations must be satisfied by all the indices. The points which in the projection (Fig. 1) lie between the intersections though along layer lines of *I* kind are caused by planes whose reciprocal lattice points do not lie in the plane ([001], [010]), as for example (223) in Fig. 2. It will be seen that the position and therefore the indices of such a point may be found by imagining the plane in which the axis [001] and point (223) lie turned about [001] until it coincides with the plane ([001], [010]), in Fig. 2. The plan in the equatorial plane (Fig. 1) is constructed for the purpose of finding the indices of such points. Perpendiculars are dropped from these points upon [010]. With the distance, from the foot of the line to the origin as radius, an arc is drawn through the plan about *O* as a center. The first two indices of the point in the elevation may be found where the arc meets a point in the plan. To be positive of this we must ascertain whether the point penetrates the sphere of reflection during oscillation. The sphere with the radius $R_0/2=250$ mm. is drawn on tracing cloth (Fig. 3). The circles representing the intersections of the layer lines of *I* kind with the sphere (*op. cit.*, Fig. 11) are also drawn in. Only eight are necessary because in Fig. 1 no point lies above layer line $s=8$. Their radii are found as indicated in Fig. 11, *op. cit.* The origin of Fig. 1 is pinned to a point on the periphery of the circle whose $R_0/2=250$ mm. Either drawing may be turned until [010] is tangent to the circle. This is the relation to each other at the starting position. The plan of Fig. 1, for a better understanding is shown in Fig. 3 where the full lines represent the starting position. Any point of the reciprocal lattice that is already inside the sphere in this position can not reflect. As the lattice is turned 30° about *O* some of its points penetrate the zero circle of the sphere. These points are able to reflect. Their projections will lie on the line [010] which contains the principal spectrum. All points in the plan of the drawing represent planes that have [001] as zone axis. The points of the reciprocal lattice above and below the equatorial plane also may penetrate the sphere and therefore may reflect. But it is obvious from Fig. 10, *op. cit.* that these points can not lie higher (or lower) than the equatorial plane than $R_0/2=250$

mm., the radius of the sphere of reflection. Therefore, a circle drawn on the elevation with radius = 250 mm. that passes through O and whose center lies on [010] contains all the points which can reflect. Another limitation for indices is imposed in the direction of the axis [001]. In Fig. 3 the position of the plan after turning through 30° is indicated by broken lines. It will be seen that no point that can reflect can have a larger angle Φ (*op. cit.*, Fig. 12) than 60°. This angle then determines the radius of the maximum limiting circle by the formula:

$$r_0 = \frac{R_0}{2} \cdot \sin \Phi \quad (op.\ cit., \text{p. } 141).$$

This radius can also be found graphically as is shown in Fig. 3, where the 60 degree line $OQ_{pmaximum}$ is the diameter of the maximum limiting circle. It is obvious then that a maximum limiting circle of $r_0 = R_0/2 = 250$ mm. would require a rotation of 45°. The limiting circle for any point can be found graphically or by calculation provided the angle Φ is known. The circle marked "minimum limiting for 30° oscillation" includes all the possible points of the plane ([001], [010]) that can reflect. These points do not move beyond $\Phi = 30°$ at any time as shown in Fig. 3.

An example will illustrate the determination of the indices. The indices for the point between 099 and 0 10 9, Fig. 1, are desired. Since $s = l = 9$, its third index will be 9. The projection of point (290) in the plan upon [010] will meet the perpendicular from the point under consideration upon [010]. The indices are therefore 299. A check on the sphere of reflection shows that the point 299 passes through it during oscillation. Another example is point 4 10 4. Examination of Fig. 3 shows that theoretically it does not pass through the sphere during oscillation but it comes within a few degrees of it. Such points sometimes give reflections. There is a possibility that this point is not 4 10 4 but 1 11 4. It can not be 0 11 4 because the sum of the indices must be even in body centered cubes.[7]

In the principal spectrum along [010] there are two reflections (040) and (080). If their α angles are substituted in the Braggs' equation

$$n\lambda = 2d \cdot \sin \alpha \qquad (22)$$

[7] See for example, Wyckoff, R. W. G.; *op. cit.*, pp. 215–16.

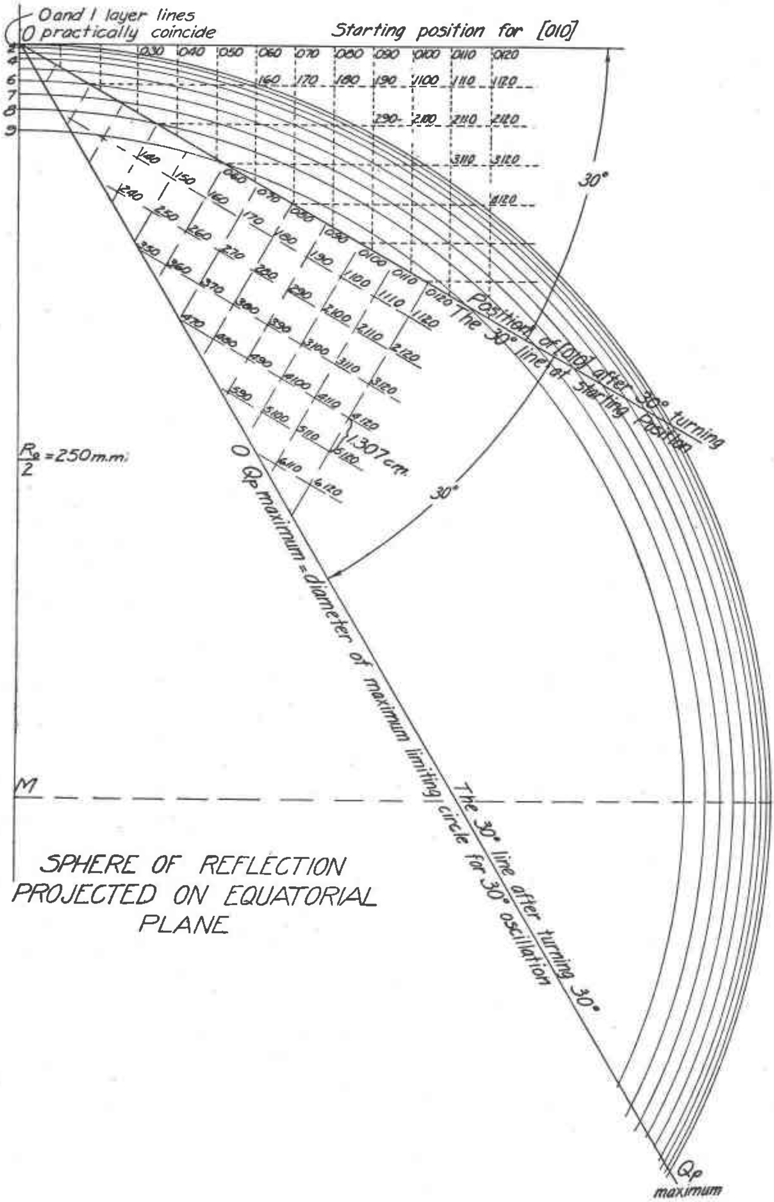
O and I layer lines
O practically coincide
Starting position for [010]
30°
Position of [010] after 30° turning
The 30° line at starting Position
1.307 cm.
O Qp maximum = diameter of maximum limiting circle for 30° oscillation
The 30° line after turning 30°
Qp maximum
M
SPHERE OF REFLECTION
PROJECTED ON EQUATORIAL
PLANE

Figure 3.

with their orders of reflection $n=4$ and 8, respectively, two values 13.539 Å and 13.595 Å for the length of the cube edge are obtained. Their average 13.567 Å is a more reliable value than that previously given. Still closer results can be obtained by precision measurements with calcite and analcite side by side on the crystal holder.[8]

All of the indices have been determined now with the exception of a few points which seem to lie on no layer lines at all. These points on examination will prove to be caused not by $k\alpha$ but by $k\beta$ ($\lambda=0.6311$ Å) radiation of molybdenum.[9] Since this radiation is much less intense, relatively strong $k\alpha$ reflections only will be accompanied by $k\beta$ reflections. This can be seen easily in the spectrograms Fig. 4 and 7. A $k\beta$ reflection always lies on a straight line connecting the corresponding $k\alpha$ reflection with the origin, and between these two points close to the $k\alpha$ reflection. It would be possible, of course, to use the $k\beta$ reflections for the construction of a reciprocal lattice if they were numerous enough by simply substituting the $k\beta$ wave length in the equations (18) and (22).

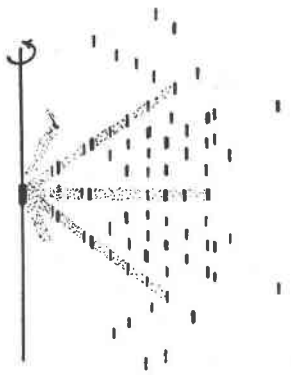

Figure 4.

Figure 7.

Figure 4. Spectrogram of analcite. Axis of oscillation parallel [$\bar{1}$01]. The direction [010] divides the spectrogram into two symmetrical parts.

Figure 7. Spectrogram of analcite. Axis of oscillation parallel to [111]. Since [111] is not normal to a plane of symmetry no symmetry as in Fig. 4 appears.

The first column of Table I contains all the indices for the spectrogram oscillated about [001]. The third column gives the

[8] Wyckoff, R. S. G.; *op. cit.*, p. 174.

[9] Bragg, W. H. and W. L.; *op. cit.* p. 57.

approximate intensities, the fourth the spacing d of equivalent planes in the space lattice. Wherever two points are symmetrical with respect to the equatorial plane like (082) and (08$\bar{2}$) any blank spaces in the columns are to be filled in with the values just above them.

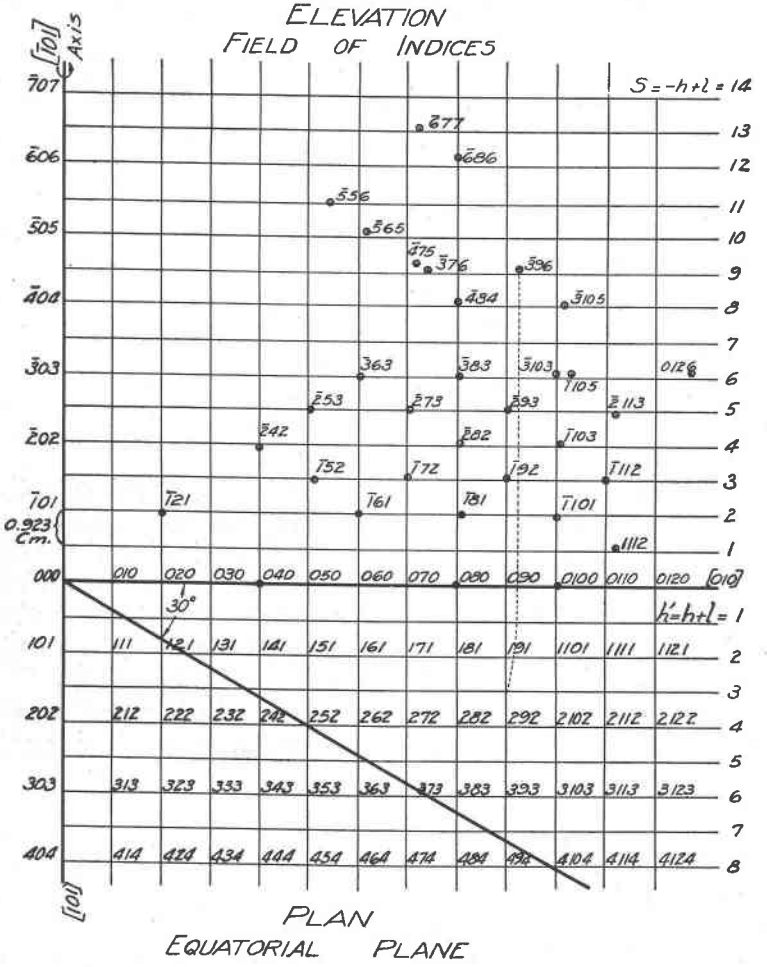

Figure 5.

Oscillation About the Face Diagonal [$\bar{1}$01]

The same face (010) as above is chosen. The directions [$\bar{1}$01] and [101] lie in it. The face is oriented as before but with the

direction $[\bar{1}01]$ parallel to the axis of oscillation. $[101]$ is the direction of the incident beam therefore at the starting position. The direction $[010]$, is normal to these directions and therefore is the abscissa in the spectrogram Fig. 4 and in the reciprocal lattice, Fig. 5, as before. The angle of oscillation is 30°. The plotted projection of the reciprocal lattice (Fig. 5) shows the layer lines of *I* kind. They are separated by only $\sqrt{2}/2$ of the distance in the reciprocal lattice about $[001]$. Therefore the primitive translation $T_{\bar{1}01}$ in the space lattice is the reciprocal of $\sqrt{2}/2$ which is $\sqrt{2}\cdot a_0$. This makes it certain that the cube is *not* face-centered. Had it been face-centered the primitive translation $T_{\bar{1}01}$ would have been $\sqrt{2}/2\cdot a_0$, and only the even-numbered layer lines would have been occupied.

The spacing along $[010]$ in the reciprocal lattice remains the same as in Fig. 1. For the finding of the indices we use the equations (19) to (21). Since $[uvw]=[\bar{1}01]$ equation (19) becomes $s=h+l=0, \pm 1, \pm 2, \pm$ integer, and (20) and (21) become:

$$h'=h+l=\text{constant}$$

$$k'=k=\text{constant}.$$

Some difficulty is encountered in finding indices for points on the odd-numbered layer lines. One would have been tempted to put the indices $[\bar{1}01]$ for example on the first layer line just above the origin 000, but equation (19) would not have been satisfied. Neither would the length $h_{\bar{1}01}$ of the vector $\mathfrak{h}_{\bar{1}01}$ in projection Fig. 5 have been the same as h_{011} in the projection Fig. 1 as it must be, if the equations (12) and (13) *op. cit.*, are correct. The fact that the lengths of vectors with the same indices are the same if the same scale has been used in the various projections constitutes an excellent check.

Let Fig. 6 represent a portion of the reciprocal lattice with indices at the corners of the cubes as shown. Let these points be projected on the plane containing the directions $[\bar{1}01]$ and $[010]$. It is seen that the points in the plane ($[101]$, $[010]$) are projected on the line $[010]$. Also those points lying on the normals to the plane ($[101]$, $[010]$) which have the intersections with this plane as origins (for example the normal 111, 012 with 111 as origin) are easily projected upon the even-numbered layer lines. This is done as illustrated in Fig. 2. But there are the points 001, 011, 021, $\bar{1}02$, and $\bar{1}12$. These are first projected upon the plane ($[101]$,

[010]) and from there upon the plane ([$\bar{1}$01], [010]) as illustrated by point 001 whose projection is *P*001. These projected points are always on odd numbered layer lines. Their indices must satisfy the equations (19) to (21) as those of the other points.

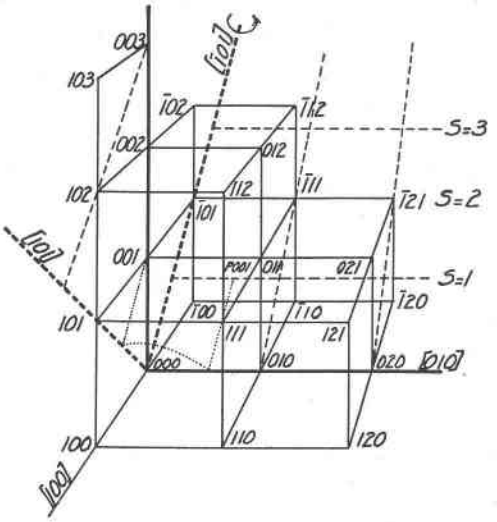

Figure 6.

Analytically the indices can be found easily. The modified equation (19) $-h+l=s$ is the equation of a plane parallel to the plane ([101], [010]). The modified equation (20) $h+l=h'$ represents a plane parallel to plane ([$\bar{1}$01], [010]). By solving these two simultaneously the equation of a straight line parallel to [010] is obtained which contains the point whose indices are wanted. This gives us the indices h and l. The point marked $\bar{3}96$ Fig. 5 is taken for illustration. Its indices are required. Projecting the point upon the equatorial plane it is found to lie on the line $h=3$. That gives us the two equations. Solving for l and h,

$$\begin{aligned} -h+l&=9 \\ h+l&=3 \\ \hline 2l&=12 \end{aligned} \qquad (19)$$

$l=6$ and $h=-3$. The index for k is read off the plan. $\bar{3}96$ are the required indices. The limiting circles as well as the sphere of reflection are used as in the projections, Figs. 1 and 3. But the circles of the sphere have been drawn with radii which correspond to layer lines with a distance of $1/T_{\bar{1}01}$ apart.

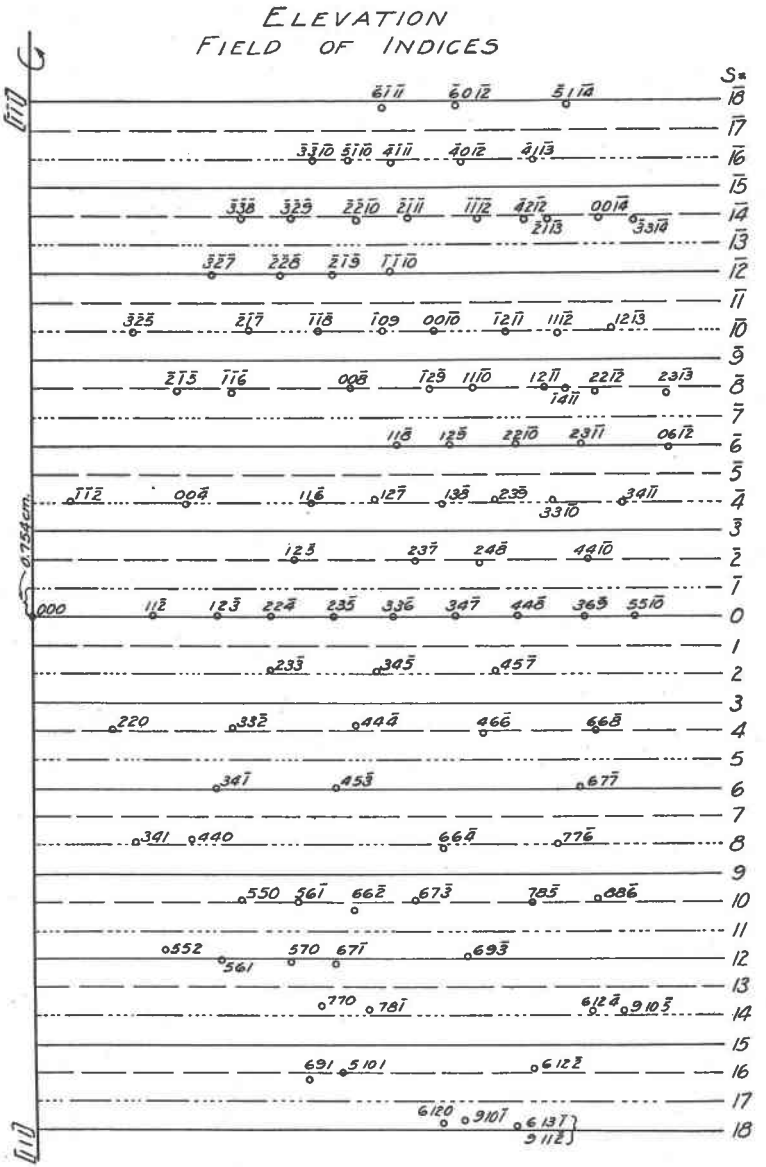

Figure 8.

Oscillation About the Body Diagonal [111].

The direction [111] lies in the face $11\bar{2}$ (Tetragonal trisoctahedron), which is well developed on analcite. $[\bar{1}10]$ is normal to [111] in this face. Let the face $11\bar{2}$ be oriented on the crystal holder in such a way that [111] is parallel to the axis of rotation and $[\bar{1}10]$ is parallel to the incident ray at the starting position. The angle of oscillation is 30°. A very large number of reflections are recorded on the photographic plate, Fig. 7. The lower half is not symmetrical with respect to the upper half since the axis [111] is not normal to a plane of symmetry. The plotting of the indices in the projection of the reciprocal lattice (Fig. 8) shows that only even-numbered layer lines of I kind are occupied. The distance between layer lines is $1/T_{111}$. But $T_{111}=a_0\sqrt{3}$. Therefore, $1/T_{111}=1/a_0\sqrt{3}=0.7545$ cm. by equation (18). Since only even-numbered lines are occupied, the primitive translation T_{111} which is the reciprocal of the distance between occupied layer lines is $a_0\sqrt{3}/2$. This shows at once that analcite is body-centered. The plan of the projection is constructed with $[11\bar{2}]$ as the abscissa and $[\bar{1}10]$ as the ordinate. This relationship is seen best in the stereographic projection Fig. 10 in which 111 is taken as the center. It will be noticed that $[01\bar{1}]$, which is equivalent to $[\bar{1}10]$, lies in the plan (Fig. 11) at 60° from $[\bar{1}10]$. Since we know the distance $h_{\bar{1}10}=(h_{0\bar{1}1})$ from the other projections it may be laid off along $[\bar{1}10]$ and $[01\bar{1}]$. A rhombic lattice is obtained in this way as shown by the full lines in Fig. 11 which is the plan of the elevation of Fig. 8. Its indices are found most easily by the equations (19), (20) and (21). They reduce to:

$s=l'=h+k+l=0$ (because the points lie in the plane.)
$h'=-h+k=0, \pm, 1\pm, 2\pm$ integer.
$k'=h+k-2l=0, \pm1, \pm2, \pm$ integer.

These equations represent planes normal to the directions [111], $[\bar{1}10]$ and $[11\bar{2}]$ respectively. l', h', k' are integers including zero which give the number of planes from the origin to the point whose indices are required. Let the point $13\bar{4}$ in the plan be taken as illustration. The equations are:

$$h+k+l=0$$
$$-h+k=2$$
$$h+k-2l=12^{10}$$

[10] In counting the planes the full as well as the broken lines are counted.

Solving for h, k and l, the indices are $13\bar{4}$.

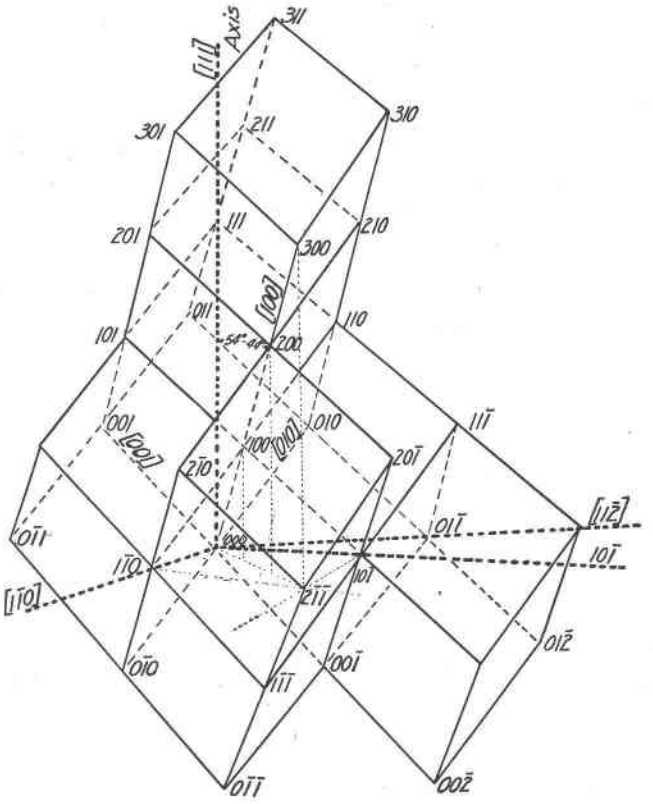

Figure 9.

With only the O plan in full lines it is not possible to find the indices of all the reflections. The portion of the reciprocal lattice reproduced in Fig. 9 shows the plane in which $[1\bar{1}0]$ $[10\bar{1}]$ and $[11\bar{2}]$ lie. By a slight oversight Fig. 9 was made the mirror image of Fig. 11 with respect to the plane ($[111]$, $[11\bar{2}]$) which is a plane of symmetry. This interchange may be seen at a glance in the stereographic projection of Fig. 10. The indices of one side can be converted into those of the other side by exchanging the first and second indices. A study of Fig. 9 shows that the points of the next plane above the ground plan do not coincide with those in the ground plan when projected perpendicularly. Neither does

the second one. The third one, however, which contains the points 111 and 300 coincides exactly. 300, for example, lies perpendicularly above $2\bar{1}\bar{1}$ of the ground plan. The points of the first plane, on the other hand, are displaced one third and those of the second plane two thirds and along the line (000, $2\bar{1}\bar{1}$) as illustrated by the projection of the points 100 and 200. This displacement really makes three plans necessary as shown in Fig. 11 by three sets of lines of different patterns. These plans may be called the *O*, the *I* and *II* plans. The *O* plan is used for the projection of indices upon every third layer line in the [111] as well as in the $[\bar{1}\bar{1}\bar{1}]$ direction of Fig. 8, in other words upon the 0, ± 3, ± 6, etc., lines. The *I* plan is used also for every third line as counted from the layer line $s=1$. The 1, 4, 7, etc., and the $\bar{2}$, $\bar{5}$, $\bar{8}$, etc., layer lines receive their indices from it. The *II* plan is used for the remaining lines 2, 5, 8, etc., and $\bar{1}$, $\bar{4}$, $\bar{7}$, etc. The indices must satisfy the equation (19) which reduces to:

$$h+k+l=s$$

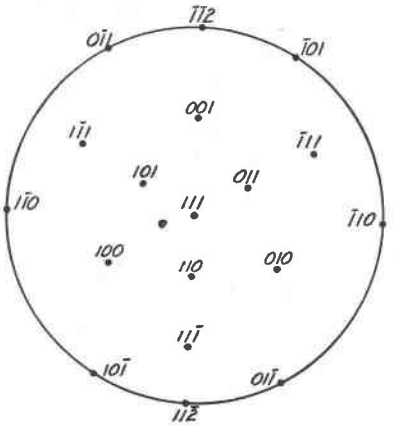

Figure 10.

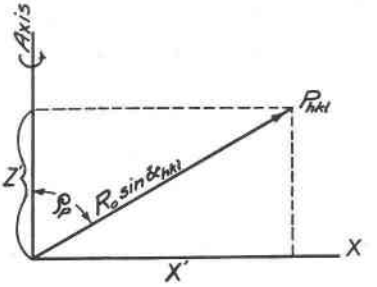

Figure 12.

The equation for layer lines of *II* kind are unreliable here because there are no marked lines in Figs. 7 and 8 parallel to the axis [111]. Inspection of Fig. 9 shows that the nearest point lying perpendicularly above another has each index increased by 1 algebraically. This is obvious because s(=number of layer lines) increases by 3 for each set of 3 layer lines. For example: A point in layer line 8 (the positive direction of 111 happens to be downward in Fig. 8) is found by projection to be above $34\bar{5}$ in the *II*

plan. Since layer line 8 is 6 lines above line 2, which corresponds to the *II* plan, two is added to each index. The indices for the point are $56\bar{3}$. A reliable check for these indices is given below.

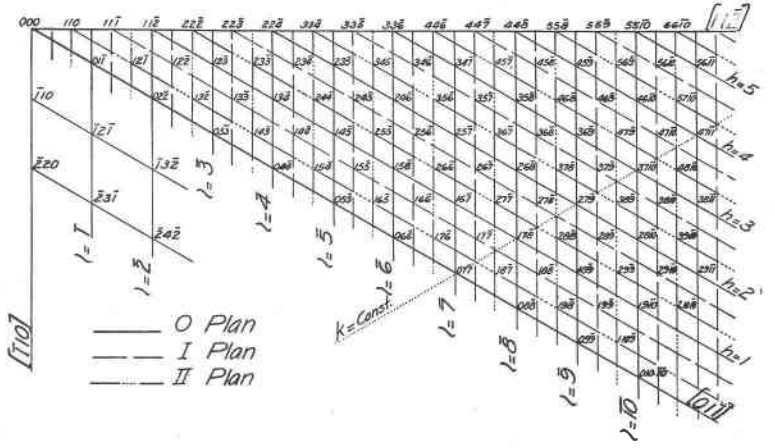

Figure 11.

Recalculation of the Angles $\bar{\phi}$ and α.

The best check on the correctness of the assigned indices is the recalculation of $\sin \alpha_{hkl}$ and $\cos \rho_{phkl}$ and $\bar{\phi}_{hkl}$, respectively, by means of these indices. By equation (22)

$$\sin \alpha_{hkl} = \frac{\lambda}{2d_{hkl}} = \frac{0.3538 \cdot 10^{-8}\text{cm}}{d_h k_l} .$$

$$d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}}$$

in the cubic system.[11]

Substituting the assigned indices in these equations (without making the indices prime) the calculated values of $\sin \alpha$ given in the fifth column of Table I are obtained. They agree closely with the measured values.[12] ρ_p is evaluated as follows. P_{hkl} is the point of the reciprocal lattice with the polar coordinates ρ_p and $R_0 \cdot \sin \alpha_{hkl}$ in Fig. 12. z' is the distance between layer lines taken s

[11] Wyckoff, R. W. G.; *op. cit.*, p. 96.
[12] Schiebold, E.; *op. cit.*, p. 251.

times. Therefore $z' = s \cdot 1/T_{u_3v_3w_3}$. The right side of the equation must be multiplied by the constant of the drawing $R_0\lambda/2$, *op. cit.* (13). Then

$$z' = \frac{R_0 \cdot \lambda \cdot s}{2T_{u_3v_3w_3}} \tag{23}$$

but $$\frac{z'}{R_0 \sin \alpha_{hkl}} = \cos \rho_P$$ see Fig. 12).

Substituting (23) for z'

$$\cos \rho_P = \frac{s \cdot \lambda}{2T_{u_3v_3w_3} \cdot \sin \alpha_{hkl}} \tag{24}$$

But by (22) $$\frac{\lambda}{2 \sin \alpha_{hkl}} = d_{hkl}$$

Substituting in (24)

$$\cos \rho_P = \frac{s \cdot d_{hkl}}{T_{u_3v_3w_3}} \tag{25}$$

It would be sufficient to compare the value of ρ_p of (25) with the ρ_p calculated from the measured $\bar{\phi}$ and $\bar{r}$ on the photographic plate. By equation (7) *op. cit.* $\bar{\phi}$ was calculated.

$$\cos \bar{\phi} = \frac{\cos \rho_P}{\cos \alpha}$$

The calculated $\bar{\phi}$ values are given in the *7th* column of Table I. They should agree to within one degree with the measured values though for points far from the origin the difference may be slightly larger.

DETERMINATION OF THE NUMBER OF MOLECULES IN UNIT CELL.

The molecular weight M of $NaAlSiO_2O_6 \cdot H_2O$ is 219.70. The density S as determined by various investigators[13] is 2.26. The volume V of the unit cell is $(13.64 \cdot 10^{-8}$ cm.$)^3$. The value 13.64 Å was determined by averaging the results of three powder dia-

[13] Doelter's HANDBUCH, *op. cit.*

grams.[14] It was taken in preference to 13.567 Å because it was an average of a great number of lines. Substituting these values in the well known formula

$$Z=\frac{V\cdot S}{M\cdot 164\cdot 10^{-24}}=\frac{(13.64)^3\cdot 2.26}{219.70\cdot 1.64}=15.92+$$

$Z=15.92+$ is the number of molecules in the unit cell. Since the number must be an integer 16 molecules is taken as the number in the cell.

The Space Group of Analcite.

Since analcite is cubic holohedral and body-centered, only the two space groups [15] O_h^9 and O_h^{10} need to be considered. The choice between these two space groups depends upon the presence or or absence respectively of certain reflections.[16] It appears that the group O_h^9 is the correct one since a number of reflections with the indices $(0k l)$, where k and l are odd, appear in the I order. Also first order reflections of (hll), where $\frac{1}{2}h$ is even and l odd, seem to be present. Unfortunately in these cases possible reflections of faces which do not violate the requirements of space group O_h^{10} can be found which give us practically as good values for the sin α and the angle $\bar{\phi}$ as those measured in the oscillation spectrograms.

Summary.

The oscillation method is used in the determination of the space group of analcite. It is shown how an oscillation diagram about a prominent crystallographic direction as an axis furnishes the primitive translation in this direction; i.e., the distance between identical atoms. For a cubic crystal three oscillation spectrograms are necessary, one with the axis parallel to the edge of the cube [001], the second parallel to the face diagonal [110], and the third parallel to the body diagonal [111]. Each spectrogram is evaluated and plotted on the reciprocal lattice. The indices for each point are found graphically. These indices are used in the

[14] Gruner, J. W.; *Zeitschr. f. Krist., op. cit.*

[15] Wyckoff, R. W. G.; The analytical expression of the results of the theory of space groups: Carnegie Institution, *Washington*, **1922.**

[16] Wyckoff, R. W. G.; The Determination of the Space Group of a Cubic Crystal. *Am. Jour. Sci.*, vol. **4**, pp. 175–187, 1922.

recalculations of the positions of the reflections in the spectrograms. If the agreement is close the indices are correct.

Analcite has the cubic holohedral lattice and seems to belong to the space group O_h^9. However, the reflections agree practically as well with the requirements of space group O_h^{10}. The correct choice between these two groups will have to be based on other considerations which can not be discussed at this time. The unit cube contains 16 molecules of $NaAlSi_2O_6H_2O$. Its edge is 13.64 ± 0.05 Å long.

TABLE I

OSCILLATION SPECTROGRAM ABOUT [001]. STARTING POSITION (010).

Indices			Layer line = s	Indensity	d	sin α		$\overline{\phi}$	
						calculated	measured	calcula.ed	measured
0	4	0	0	1	3.410	.1037	.1045	90°00	90°00
0	8	0	0	1–2	1.076	.2072	.2082	90°00	90°00
1	10	1	1	2	1.351	.2619	.2627	84°06	84°24
1	10	$\bar{1}$	$\bar{1}$	2			.2620		83°30
0	2	2	2	3	4.823	.0733	.0735	44°51	44°54
0	6	2	2	5	2.157	.1640	.1636	71°45	71°42
0	6	$\bar{2}$	$\bar{2}$	5			.1639		71°42
0	8	2	2	3	1.658	.2134	.2139	75°36	76°36
0	8	$\bar{2}$	$\bar{2}$	3			.2150		74°48
1	9	2	2	3	1.475	.2398	.2416	77°08	77°30
1	9	$\bar{2}$	$\bar{2}$	3			.2410		76°30
0	10	2	2	5	1.351	.2646	.2654	78°09	78°36
0	10	$\bar{2}$	$\bar{2}$	5			.2658		77°36
1	11	2	2	5	1.215	.2911	.2910	79°16	79°42
1	8	3	3	3	1.586	.2230	.2232	69°02	69°36
1	8	$\bar{3}$	$\bar{3}$	3			.2238		67°48
1	10	3	3	4	1.300	.2722	.2726	72°43	73°12
1	10	$\bar{3}$	$\bar{3}$	4			.2719		71°42
0	4	4	4	2–3	2.412	.1467	.1460	44°21	44°54
0	6	4	4	2	1.889	.1873	.1868	55°41	56°18
0	6	$\bar{4}$	$\bar{4}$	2			.1874		55°00
1	7	4	4	4	1.678	.2108	.2090	59°46	61°18
1	7	$\bar{4}$	$\bar{4}$	4			.2113		58°30
0	10	4	4	4	1.266	.2794	.2801	67°15	67°18
0	10	$\bar{4}$	$\bar{4}$	4			.2810		66°24
4	10	4	4	5	1.187	.2981	.3004	68°39	69°48
1	6	5	5	4	1.732	.2043	.2048	47°47	50°48
1	6	$\bar{5}$	$\bar{5}$	3			.2048		48°18
1	10	5	5	4	1.215	.2911	.2910	61°10	63°00
1	10	$\bar{5}$	$\bar{5}$	4			.2910		61°42
1	5	6	6	4	1.732	.2043	.2051	38°53	39°54
0	6	6	6	3	1.607	.2201	.2193	43°33	43°06
0	8	6	6	2–3	1.364	.2594	.2606	51°36	52°00
0	8	$\bar{6}$	$\bar{6}$	3			.2599		51°06
1	9	6	6	4	1.255	.2818	.2810	54°51	55°48
1	9	$\bar{6}$	$\bar{6}$	4			.2810		54°54
0	10	6	6	5	1.166	.3033	.3021	57°25	57°36
1	12	6	6	5	1.016	.3480	.3461	61°30	62°18
1	4	7	7	3	1.678	.2108	.2119	28°10	29°24
1	8	7	7	3	1.277	.2769	.2773	46°48	47°42
1	8	$\bar{7}$	$\bar{7}$	3			.2773		46°12
1	7	8	8	3	1.277	.2769	.2773	38°45	39°30
1	7	$\bar{8}$	$\bar{8}$	4			.2773		38°00
1	11	8	8	4	1.016	.3480	.3537	51°04	51°48
2	9	9	9	4	1.058	.3342	.3346	42°13	43°12
2	9	$\bar{9}$	$\bar{9}$	4			.3341		41°18
2	7	7	7	3	1.351	.2619	.2642	45°12	45°12
2	7	$\bar{7}$	$\bar{7}$	2			.2647		43°30