THE THERMO-OPTICAL PROPERTIES OF HEULANDITE*

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Abstract

Heulandite shows two characteristic changes in its optical properties with rising temperature, a rotation of the optic plane and a variation in the size of the optic angle. If these changes in the optical properties are plotted against the temperature, the curves fall into two distinct sections. The first portion, 25°-190° C, is characterized by a gradual and progressive rotation of the optic plane and by a decrease in the size of the optic angle. The second portion shows a rapid rotation of the optic plane and an increase in the optic angle. This change in the character of the curves is correlated with the development of the three molecule hydrate. The uniaxial point, which has been reported previously, is only apparent and is due to the rapid rotation of the optic plane when the optic angle is very small.

A similar change in the optical properties may be observed by dehydrating the crystals at room temperature with concentrated sulphuric acid. Laue diagrams taken at various temperatures show a gradual breaking down of the crystal structure if the crystals are dehydrated at a temperature above 190° C. This breaking down of the structure cannot be observed immediately after dehydration, as the original structure persists in a metastable condition, but the change is very pronounced a few months after dehydration.

INTRODUCTION

Unlike most hydrated salts, the zeolites do not break down and lose their crystalline form when dehydrated. As the dehydration progresses the crystals gradually become cloudy and finally opaque, but they regain their original transparency by absorbing moisture from the air. A crystal which has been dehydrated until it is opaque will likewise become transparent if it is allowed to absorb oil, alcohol, or some other organic liquid.

These peculiar properties of the zeolites were observed by early investigators and were attributed to a sponge-like structure of the crystals. Johnsen[1] has explained these phenomena by a phase of "solid solution," while Doelter[2] has considered this action to be due to "colloidal adsorption" of the water by the crystal.

In 1915 A. Beutell and K. Blaschke[3] attempted to correlate the behavior of the zeolites with that of the characteristic hydrated salts. For desmine, a zeolite dimorphous with heulandite, they found

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[1] Die Anomalen Mischkristalle: *Neues Jahrb. f. Min.*, **2**, 93-138 (1903).

[2] *Phys. Chem. Mineralogie*, p. 179, (**1905**).

[3] Das Wasser im Desmin ist chemisch gebunden: *Centr. f. Min.*, 4-11, (**1915**).

that the dehydration curve was discontinuous. The curve, which was constructed by plotting water content against the temperature, was step like, showing no loss of water through certain temperature intervals. In 1919 G. Stoklossa[4] carried the same relationship over into the rest of the zeolites. His methods were similar, consisting of the determination of the water driven off with increasing temperature, and indicated significant "Haltepuntke" whenever the water was present in molecular ratios. At most of these points he examined cleavage fragments under the microscope and noted the variations in the optical properties as further evidence of the existence of definite hydrates. The uniaxial point of heulandite, which Rinne[5] had previously reported as existing between 80°-100° C, he attributed to the "Kompensationerscheinung" between the 9 molecule hydrate and the 10 molecule hydrate (doubled formula) whose transition point he had found to be at 80° C.

Weigel's[6] work which was published in the same year gave results of a decidedly different character. He found that the water of heulandite was driven off gradually and not in molecular ratios. The curve of dehydration was reversible up to 180° C. when a definite breaking point was reached which indicated the formation of a new hydrate. Scheuman[7] gave similar results but established 186° C. as the temperature at which the three molecule hydrate was formed.

In 1921 Beutell[8] brought forth some new experimental data in a series of two articles upon "Die Wasserbindung im Heulandit" to verify his previous work. Weigel[9] published two articles upon "Zur Frage der Wasserbindung in den Zeolithen" in reply to Beutell. He introduced no new experimental data but referred to the confirming results of Scheuman which had appeared in the meantime.

Unfortunately, there is very little data available upon the vapor pressures of the hydrated silicates. Tammann[10] has determined the

[4] Ueber die Natur des Wassers in dem Zeolithen: *Neues Jahrb. f. Min.*, 1-64 (**1919**).

[5] Ueber Faujasit und Heulandit: *Neues Jahrb. f. Min.*, **2**, 17-38 (1887).

[6] *Sitz. Ber. Ges. z. Beforderung d. ges. Naturw. Marburg*, 48-63, (**1919**).

[7] Uber die Wasser die Heulandit: *Verh. d. Sdchs. Akad. Wiss., Leipzig, Math-Phys. Kl.*, 1-113 (**1921**).

[8] *Centr. f. Min.*, 694-702, 721-734 (**1921**).

[9] *Centr. f. Min.*, 164-178, 201-208 (**1922**).

[10] Ueber die Dampfspannurg von Kristallierten Hydraten: *Z. Phys. Chem.*, **27**, 323-336 (1896).

vapor pressures of a number of the zeolites, including thomsonite, natrolite, phillipsite, harmotone, and chabazite, by allowing the crystals to stand over known concentrations of sulphuric acid. He plotted the vapor pressures against the loss of water and obtained a continuous curve. Upon the basis of Tamman's work, Findlay[11] uses the zeolites as typical examples of solid solution somewhat similar to the absorption of hydrogen by palladium.

The variations in the optical properties of heulandite with an increase in temperature has been noted by DesCloizeaux,[12] Mallard[13] Klein,[14] Rinne,[15] Stoklossa,[16] and Weigel.[17] In all of these cases the observations were made under the microscope, upon sections which had been previously heated, and gave conflicting results, because no attempt was made to observe the changes continuously under well controlled temperatures. These changes have been generally ascribed to the loss of water.

The purpose of this investigation is to measure the variations in the optical properties of heulandite which accompany an increase in temperature and to determine what relationship these changes bear to the dehydration of the mineral.

EXPERIMENTAL DATA

The optical properties of heulandite were determined upon the large well developed crystals found in the amygdaloidal cavities of the basaltic rocks at Berufiord, Iceland. These crystals varied in size from 5 to 15 mm. wide, 10 to 30 mm. long, and 5 to 15 mm. thick. The excellent cleavage parallel to (010) gave nearly perfect sections 1 to $1\frac{1}{2}$ mm. thick. The indices of refraction were determined with the Abbe refractometer upon a polished pinacoidal cleavage section at 25° C. and gave for sodium light the following values: $\alpha = 1.4991$, $\beta = 1.5008$, $\gamma = 1.5052$.

These values give a calculated angle of 73° 20′ for the apparent angle (2E) of the optic axes in air. The measured value for the same section at 25° C. was 74° 38′. The angle of the optic axes

[11] THE PHASE RULE, p. 140, (1923).

[12] MANUEL DE MINERALOGIE, p. 426, (1862).

[13] De l'action de la Chaleur sur la Heulandite: *Bull. Min. Fr.*, **5**, 255-260, (1882).

[14] Beiträge zur Kenntniss der optischer Aenderung in Krystallen unter dem Einflusse der Erwarmung: *Z. Kryst.*, **9**, 38-72 (1884).

[15] Ueber Faujasit und Heulandit: *Neues Jahrb. f. Min.*, **2**, 17-38 (1887).

[16] Ueber die Natur. des Wassers in dem Zeolithen: *Neues Jahrb. f. Min.*, 1-64 (1919).

[17] *Sitz. Ber. Ges. z. Beforderung d. ges. Naturw. Marburg*, 48-63 (1919).

varied slightly from crystal to crystal but all measured values fell between the limits of 68° and 76°. The orientation of the optical directions at 25° C. is shown in Figure 1. The acute bisectrix is parallel to the b-axis and the crystal is positive.

The analysis was made upon the same Berufiord, Iceland, crystals that were used for the determination of the optical properties. Column 1 shows the composition as determined by analyses at 25° C. and column 2 gives the theoretical composition calculated from the formula $CaO.Al_2O_3.6SiO_2.5\frac{1}{2}H_2O$.

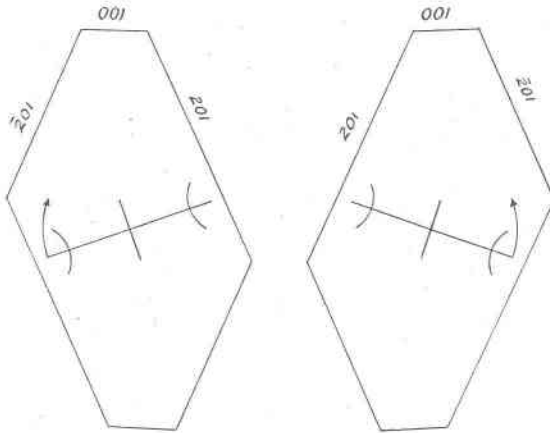|	1.	2.
SiO_2	58.55	57.66
Al_2O_3	17.64	17.86
CaO	5.82	8.91
SrO	0.59	——
Na_2O	1.25	——
K_2O	0.81	——
H_2O	15.88	15.57
	100.54	100.00

Fig. 1

OPTICAL ORIENTATION OF HEULANDITE

Heulandite has a very low double refraction, $\gamma—a=0.0061$ and $\beta—a=0.0017$. An interference figure is not dependent upon the absolute magnitude of the double refraction but rather upon the relative value of the double refraction in different directions through the crystal. Hence, a small change in the magnitude of the indices

of refraction will produce a relatively large change in the interference pattern. This is more pronounced in crystals of low double refraction than in those with high double refraction. In any consideration of the optical changes in heulandite it is well to bear this fact in mind, because large variations in the size of the optic angle and in the position of the optic plane may be brought about by slight distortions in the structure of the crystal.

The size of the optic angle and the position of the optic plane of heulandite are dependent upon the temperature and the state of of hydration of the crystal. With an increase in temperature the optic plane rotates counter-clockwise upon (010) and clockwise upon ($0\bar{1}0$). The acute bisectrix remains perpendicular to these faces.

DETERMINATION OF THE OPTICAL ROTATION

The rotation of the optic plane with an increase in temperature was measured directly from the interference figures by using the Groth axial angle apparatus. To measure the rotation of the optic plane with the crystal mounted in an oil bath it is necessary to rotate the horizontal cross hair to follow the movement of the optic plane while the crystal remains stationary. The analyzing tube was fitted with a graduated circle reading to $5'$ which measured this rotation. The polarizing and analyzing nicols were then connected so that they would rotate simultaneously and independently of the cross hairs.

The crystals were studied in an electrically heated oil bath, which was mounted between the condenser and the objective. This bath was constructed of brass and was 22 cm. long, 5 cm. deep, and $2\frac{1}{2}$ cm. wide. The bath was enclosed in an asbestos fiber board case to prevent the radiation of heat. The thermometers were calibrated with a standard thermometer inserted in the same position as the crystal section and were corrected for stem emergence.

DETERMINATION OF THE OPTIC ANGLE

The angle of the optic axes for any crystal may be determined directly by mounting the crystal horizontally and rotating it so that the optic axes will come successively to the cross hairs. This will give the angle of the optic axes at room temperature but it will not give the true angle if the plane of the optic axes has rotated from the horizontal. A close approximation of the sine of H (2H being the observed angle of the optic axes in oil) may be made by

dividing the sine of half the angle of rotation, which is necessary to bring the optic axes successively to the cross hairs, by the cosine of the angle of rotation of the optic plane. Because of the inaccuracies of this method, the angle was calculated from the photographs of the interference figures.

Mallard[18] has shown that for any given lens system the distance from any point in the interference figure (as formed in the rear focal plane of the objective), to the center of the field is proportional to the sine of the angle formed by the axis of the microscope and a ray of light striking at that point. If the acute bisectrix is parallel to the axis of the microscope (emerges in the center of the field) then the distance from the center of the field to one of the optic axes is proportional to the sine of half the angle of the optic axes. From a section whose optic angle is known, a constant K (Mallard Constant) for the lens system may be computed from the formula $K = \dfrac{D}{\sin H}$. By applying this constant K, the value of an unknown optic angle may be computed by measuring its distance from the center of the field. This is the principle upon which the engraved scale which is inserted in the rear focal plane of the objective of the Axial Angle Apparatus is made. Becke[19] has developed a graphic method based upon the same principle.

By carrying this principle still further it may be used in calculating optic angles from photographs. The crystal is mounted with the optic plane horizontal and the optic angle measured by rotating the crystal. The interference figure is then centered in the field and photographed. From the known optic angle and the distance of the optic axes from the center of the photograph, a constant K may be calculated for the lens systems of the objective and of the camera, and for the distance of the photographic plate from the crystal. Then, by applying this constant to photographs taken with the same lens systems similarly focused, the unknown optic angles may be calculated.

The calculation of the optic angles from the photographs of the interference figures is very accurate because the distances are measured upon the photographic images which are enlarged four

[18] *Bull. Soc. Min. Fr.*, **5**, 77-87 (1882); also F. E. Wright, THE METHODS OF PETROGRAPHIC-MICROSCOPE RESEARCH, p. 148, (**1911**).

[19] *Tschermak's Min. petr. Mittheil.*, **14**, 563 (1894); **16**, 180 (1896).

or five diameters over the size of the image observed directly with the conoscope. With long exposures the photographs are more distinct than the figures observed with the eye. Some of the photographs in Figures 5 and 5a were taken with exposures of fifteen minutes.

The values for the optic angles calculated by this method were the observed angles in oil and must be converted to 2E, the observed angle in air by multiplying the sine of the angle in oil by the index of refraction of the oil used in the bath. Paraffine oil was used because of its chemical inactivity and its high boiling point. The index of refraction of paraffine oil decreases rapidly with an increase in temperature so its index was measured at higher temperatures.

DETERMINATION OF THE INDEX OF REFRACTION OF PARAFFINE OIL

The indices of refraction of paraffine oil for sodium light at different temperatures were determined by the method of minimum deviation. The oil was heated in a hollow glass prism which was mounted upon the stage of the goniometer in an asbestos board chamber which was heated by a resistance unit. A thermometer was immersed directly in the oil and its readings were corrected for stem emergence. Plotting the values of the index of refraction against the temperature gave the index as a straight line function of the temperature.

INDICES OF REFRACTION OF PARAFFINE OIL. (MINIMUM DEVIATION)

Temperature C.	Index of Refraction
27	1.4813
45	1.4766
62	1.4712
75.5	1.4666
93.8	1.4619
109	1.4570
119.2	1.4537
130	1.4517
152	1.4441
156.5	1.4436
186	1.4371
203	1.4277
206	1.4290
212	1.4278

METHODS OF PROCEDURE

With a gradual increase in temperature a crystal of heulandite will slowly dehydrate and rotate the plane of the optic axes. This dehydration will proceed progressively from the surface of the crystal to the center and will give a series of lamellae with slightly different orientations. However, if the temperature increase is too rapid this development of lamellae is very pronounced, the brushes of the interference figure will disappear, and give only the lemniscates of the interference figure as is shown in Figure 5a, L. The brushes of the interference figure are formed where the optical directions of the crystal are parallel to the vibration directions of the two nicols. If, then, because of the different orientations of the lamellae, the crystal is not optically homogeneous, the brushes will disappear. By regulating the rate of increase of temperature to a point where the brushes are always visible, uniform conditions will prevail in the crystal.

The preliminary observations in this investigation were wholly of a qualitative nature. A number of sections were made from different crystals and their optical properties were observed through the same temperature intervals by alternately raising and lowering the temperature. This gave a general knowledge of the behavior of the crystals at different temperatures. With this general knowledge of the crystals as a background, measurements of the optic plane and optic angle were made through the whole temperature range up to 300° C. Preliminary curves of the optical properties were plotted from these values. The final determinations were made upon the clearest and best developed crystals and photographs were taken at those points which the preliminary work had revealed as significant.

A crystal which has been dehydrated in oil can be restored to its original condition by dissolving the oil in alcohol and then boiling in water to remove the alcohol. One section was treated in this way twice and the same variation in optical properties was observed three successive times. Observations were also made through the short temperature intervals which can be obtained with water and alcohol baths. Heulandite is not attacked by concentrated sulphuric acid but it is rapidly dehydrated. These sections can also be restored to their original condition by boiling them in water.

GENERAL CHARACTERISTICS OF THE CURVES
OF OPTICAL PROPERTIES

The curve, obtained by plotting the rotation of the optic plane against the temperature, falls into two general sections. The first section of the curve covers the temperature interval between 25°-177° C. through which the rotation is slow and uniform. The total rotation in this interval is 19° and when plotted with the temperature gives a perfectly straight line (Figure 2). The second section is characterized by a rapid rotation of the optic plane which reaches a maximum of 120° at a temperature of 320° C.

If we examine the curve obtained by plotting the size of the optic angle with the temperature, we find the same general division into two distinct phases (Figure 3). The first effect of increasing the temperature is to enlarge slightly the optic axial angle but this is followed by an abrupt and rapid decrease in the size of this angle which reaches a minimum at a temperature of 190° C. The second phase is characterized by a rapid increase in the optic angle. At 300° C. the optic axes have passed out of the field of vision and the optic angle has value of approximately 120°.

REVERSIBILITY OF THE CURVES OF THE OPTICAL PROPERTIES

Reversibility of the curves of the optical properties is only possible when a decrease in temperature is accompanied by rehydration. If a crystal of heulandite is partially dehydrated in air and then allowed to cool, it will slowly return to its original state of hydration by absorbing moisture from the air, but if it is heated in an oil bath this rehydration by the absorption of moisture is manifestly impossible. Hence, upon cooling to room temperature we may determine the optical constants of a partially dehydrated crystal under the same conditions under which we originally determined the optical constants of the hydrated crystal. Any changes observed upon reheating the crystal will be due to the variation in temperature alone, unless the heating is carried to a point where further dehydration will take place. Figure 4 is a graphical representation of the changes in the position of the optic plane and in the size of the optic angle, which accompany heating to definite temperature, cooling in oil to prevent rehydration, and then reheating to a still higher temperature.
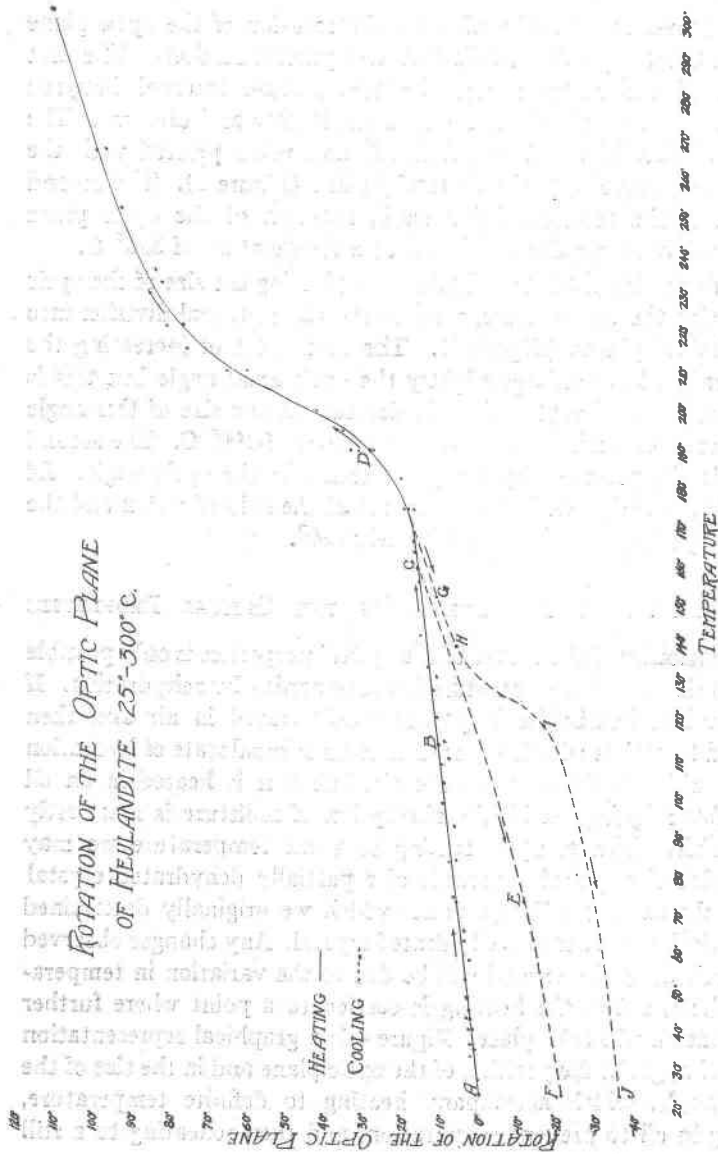
ROTATION OF THE OPTIC PLANE
OF HEULANDITE 25°–500° C.

HEATING ——
COOLING ----

ROTATION OF THE OPTIC PLANE

TEMPERATURE

FIG. 2.

VARIATION IN THE OPTIC ANGLE
OF HEULANDITE — 25°-300° C.

HEATING ——
COOLING - - - -

VALUES FOR OPTIC ANGLE ABOVE
200° ARE ONLY APPROXIMATE.

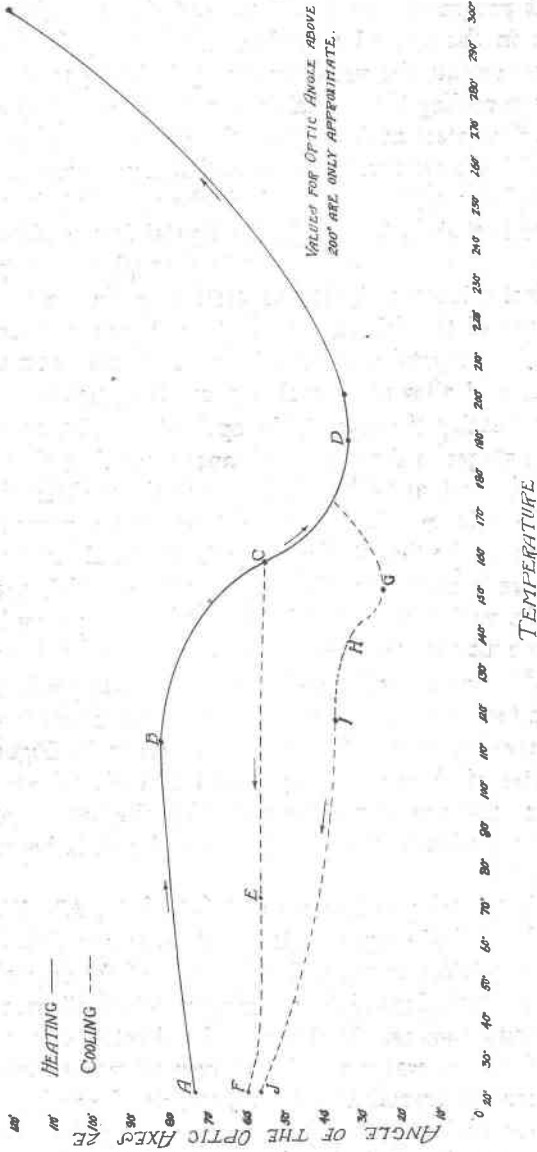ANGLE OF THE OPTIC AXES 2E

TEMPERATURE

FIG. 3.

If we start at A, Figure 4, and pass along the diagonal ABCD, each step represents successive intervals of rising temperature. The change is progressive from 25° to 300° C. and shows a regular variation in the optical directions of the crystal. Each vertical column represents the variations in optical properties that will be found upon cooling the crystal from any definite temperature. For example, if we start at A and pass along the diagonal to the vertical column with the caption 125°, we shall observe that the plane of the optic axes has rotated counter-clockwise and that the angle of the optic axes is slightly larger. If the crystal is now allowed to cool, the optic plane will pass successively through the stages shown in the vertical column and become stationary in the position given at the base of the column. This then, is the position of the optic plane for a crystal which has been dehydrated at a temperature of 125° C. and allowed to cool to room temperature.

Upon reheating the crystal, the optic plane will pass through the successive stages in the reverse manner from that observed during the cooling, until, at 125° C. it will be in the position shown at the top of the column. With further heating the movement of the optic plane will be that shown along the diagonal. If the increase in temperature is carried to 175° C. and the crystal is again allowed to cool, the variations shown in the 175° column may be observed in the same manner as those observed in the 125° column.

The 25° temperature interval used in this diagram is an arbitrary unit. If a temperature interval of 12½° were chosen it would show the intermediate stages between those given in Figure 4. The whole series of observations indicated in each column cannot be seen upon any one crystal because the alternate expansion and contraction gradually destroys the crystal and it becomes nearly opaque.

Through the temperature range 25°-100° C., AB, Figure 4, the curve of the optical properties is completely reversible. This upper limit of reversibility is not a characteristic of the crystal itself, but rather of the conditions of the experiment, which allows rehydration to accompany cooling. If the crystal is heated to a temperature below 100° C. the water which is driven off will remain as a thin film between the crystal and the oil, and will be reabsorbed by the crystal upon cooling. The upper limit is not definitely located at 100° C. but may be reached at a somewhat lower temperature if the

crystal is held at that temperature for a considerable length of time. In one case where the temperature was held constant for three days at 85° C. the optic plane did not return to its original position upon cooling, but showed the behavior which is characteristic when the water is permanently lost to the crystal.
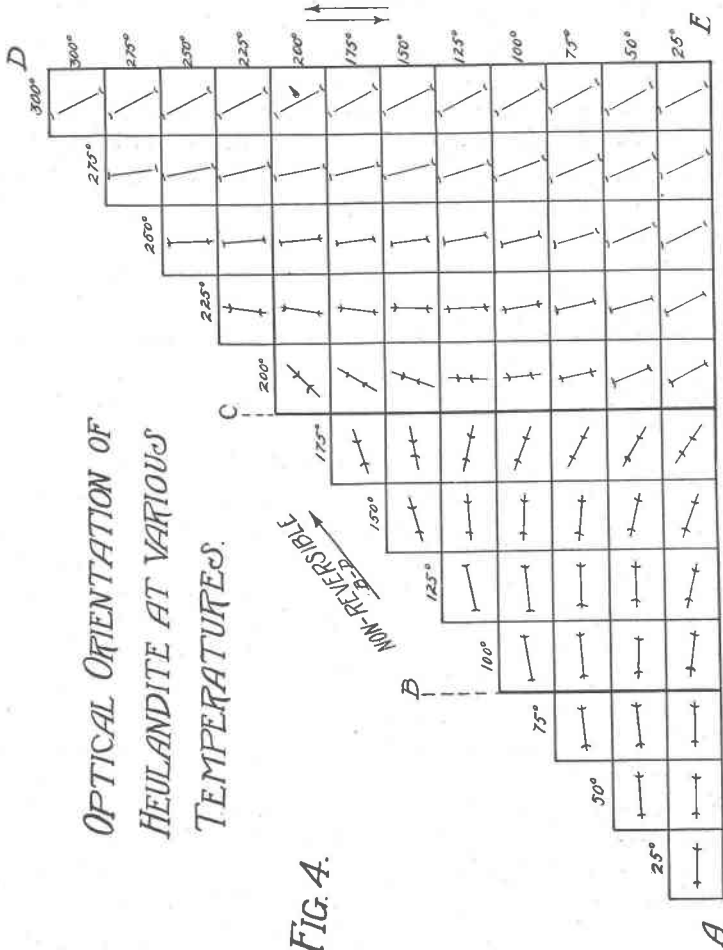

OPTICAL ORIENTATION OF HEULANDITE AT VARIOUS TEMPERATURES.

FIG. 4.

## MEASUREMENT OF THE CHANGE IN DOUBLE REFRACTION

It has been previously noted that the double refraction of heulandite is very low. This double refraction can be measured with exactness only under ideal conditions, but once measured, it will furnish a basis by which comparative values for the double refraction at higher temperatures may be determined. In a biaxial interference figure, with crossed nicols, the leminiscate interference bands are formed where the phasal difference of converging monochromatic light is one wave length or a multiple of one wave length. The phasal difference of two rays of light emerging from the surface of a crystal is dependent upon the distance they have travelled through the crystal and upon the double refraction of the mineral. Therefore, upon the same section or upon sections of equal thickness, the double refraction is directly proportional to the number of interference bands surrounding the optic axes. The optic axes and the acute bisectrix are perpendicular, respectively, to vibration directions of β and a, so therefore, the number of rings between an optic axis and the acute bisectrix is proportional to the double refraction β-a.

All of the photographs shown in Figures 5 and 5a were taken upon the same section which was 1.30 mm. thick, and when the interference figure was in the 45° position at 25° C. there were $3\frac{1}{2}$ interference bands between the optic axes and the acute bisectrix. The value of the double refraction β-a at this temperature is 0.0017, so each band represents an approximate double refraction of 0.0005. This method is only approxmiate because the fractions of an interference band must be estimated.

THE APPARENT UNIAXIALITY POINT

DesCloizeaux and Rinne have reported that heulandite became uniaxial at temperatures of 100° and 80° C., respectively. Their observations were made under the microscope and were purely of a descriptive nature. Under these conditions it would be very easy to give this interpretation to the facts observed during the the rotation of the optic plane of a crystal whose optic angle was small.

This may be readily seen from the photographs G, H, I, and J, Figure 5a, which were taken at the successive temperatures of 154°, 141°, 121°, and 25° C., with the nicols horizontal and vertical. In G the optic plane is nearly horizontal and the brushes lie in the upper

FIG. 5a.
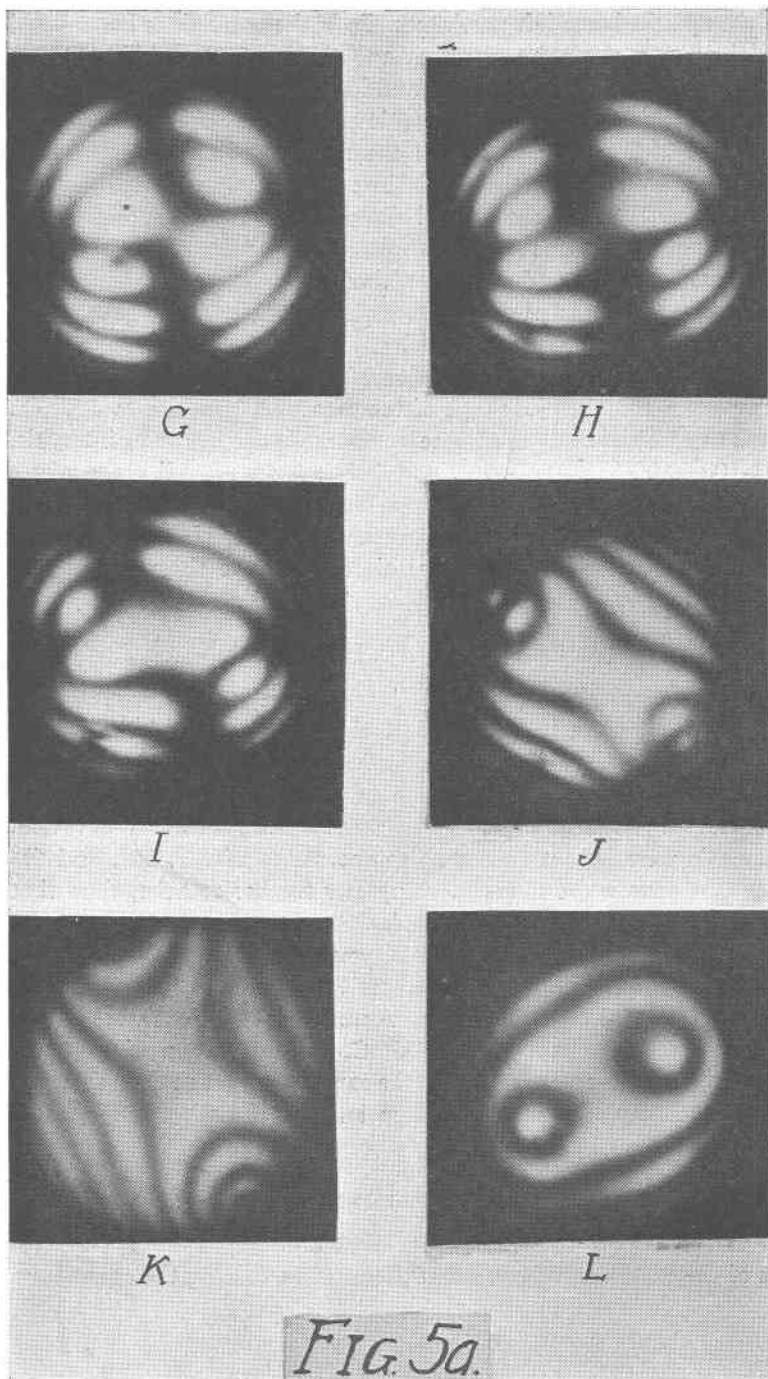
right and the lower left quadrants. In H the optic plane has rotated slightly in a clockwise direction and the brushes have just begun to separate into the upper left and lower right quadrants. I and J show a further rotation of the optic plane and also an increase in the size of the optic angle. If the rotation of the optic plane is followed by rotating the nicols in such a manner that they are always at 45° with the optical directions of the crystal, the true biaxial nature of the crystal is always apparent. It can also be observed from the photographs that the interference bands surrounding the optic axes are always elliptical, while in the case of uniaxiality they should be circular.

For a more detailed description of the variations in the optical properties through the range of temperatures from 25° to 300° C., it is convenient to divide the temperature range into four intervals, 25-100°, 100-177°, 177-192°, and 192-300° C. In all cases where variations in the size of the optic angle are given, the numerical values refer to 2E, the apparent angle in air, although in most cases these values have been calculated from the observed angle in oil.

OPTICAL CHANGES IN THE INTERVAL 25°-100° C.

The optical changes in this interval are not very great and equilibrium is reached in a relatively short period of time. If a crystal is rapidly heated and then held at a constant temperature the rotation reaches a maximum in five to ten minutes and will remain indefinitely at that point. To verify this observation, crystals were held at constant temperatures of 32°, 50°, and 67° for two days without experiencing any further rotation than that observed shortly after they reached that temperature.

The total rotation through this temperature interval is $9\frac{1}{2}°$ and the angle of the optic axes increaes 7°. There is no appreciable change in the double refraction. A number of sections were heated in water to a temperature of 95° C. and a rotation of $6\frac{1}{2}°$ was observed. This rotation was in the same direction as that observed in oil. The maximum rotation in an alcohol bath was $5\frac{1}{2}°$ at a temperature of 74° C.

OPTICAL CHANGES IN THE INTERVAL 100°-177° C.

The rotation of the optic plane through this temperature interval is of the same character as that observed in heating the crystals up

to a temperature of 100° C. The curve obtained by plotting the rotation with the temperature is a continuation of the straight line established in the previous interval. The optic angle shows a slight increase in size and reaches a maximum at about 115° C. when it begins to diminish rapidly. The most marked change is observed in the enlargement of the leminiscate interference bands due to the decrease in the double refraction. This is readily observed in the photographs B and C (Figure 5). In B there has been no perceptible change from the number of rings in A which shows the same crystal at room temperature, but the change in C is very pronounced. Here only $1\frac{1}{2}$ bands lie between the optic axes and the acute bisectrix while in the original photograph A there were $3\frac{1}{2}$ bands, which shows that the double refraction is less than one-half of the original value.

In Figures 2 and 3, two cooling curves are drawn which correspond to the similarly lettered photographs in Figures 5 and 5a. CEF shows the effect of cooling from a temperature of 161° C. to 25° C. There is a very pronounced rotation of the optical plane but practically no change in the size of the optic angle. The double refraction increases slightly between C and E, but remains fairly constant between E and F. These three photographs follow closely the changes depicted graphically in Figure 4, 150° vertical column.

More striking changes are shown by the cooling curve GHIJ and the corresponding photographs, although for this curve the crystal was heated to a temperature only 16° higher than for the curve CEF. In G, H, and I, there are no interference bands between the optic axes and the acute bisectrix, and the double refraction is therefore less than one-fourth of the double refraction shown in the photograph A The angle of the optic axes in G is 24°, while the original value was 74°.

A comparison of the photographs A, F, and J taken at 25° C., but in different stages of hydration, shows:

	Rotation	Optic Angle	Double Refraction
A	—	74°	0.0017
F	21°	61°	0.0010
J	36°	57°	0.0008

These changes are produced by heating a crystal to different temperatures and then cooling, and are therefore changes due to

FIG. 5.
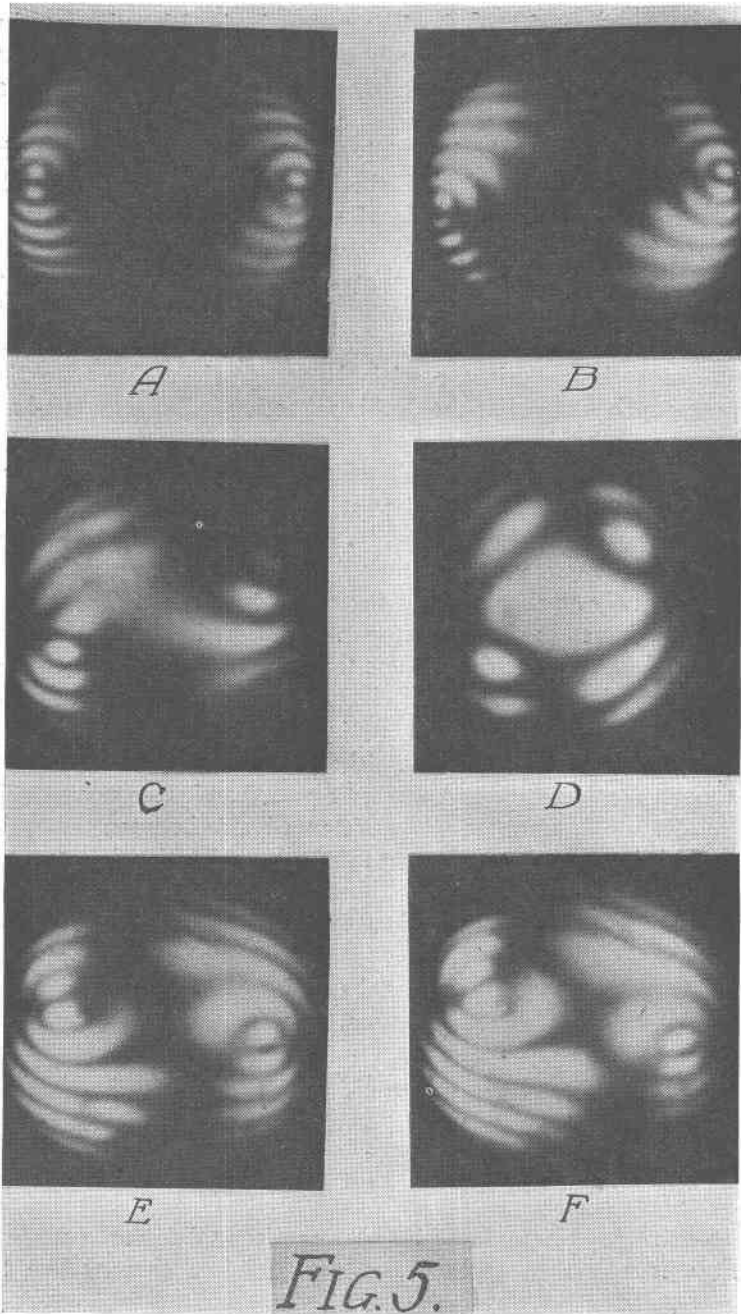
dehydration alone The more striking changes observed at higher temperatures are due both to dehydration and to temperature effects. These resultant changes in the optical properties are more readily observed in Figure 4, A to E, where they are graphically illustrated

Optical Changes in the Interval 177°-192° C.

The transition point between the gradual and uniform rotation of the optic plane and the more rapid rotation at higher temperatures lies in this temperature interval. Weigel places the transition point at 180° C. while Scheuman places it at 186° C. A study of the optical properties also shows that a definite structural change is taking place. Observations which were easily made at lower temperatures become very difficult due to anomalous conditions which develop in the interference figures. Such interference figures as the one shown in the photograph L Figure 5a, become very characteristic.

The lamellar structure in which some of the lamellae have different orientations from the others is revealed in the absence of of brushes. A difference in double refraction around the two optic axes is shown by a variation in the distance between the interference bands surrounding the axes. The anomalous character of this interference figure is not so pronounced as in most of the cases when the changes were so rapid that it was impossible to photograph them. This photograph was taken with a twelve minute exposure and a movement of the figure during the exposure is shown by the blurring of the bands.

At higher temperatures the conditions become more stable and it is possible to obtain photographs of normal interference figures such as D, Figure 5, which was taken at a temperature of 192° C.

A distinct difference in the character of the changes produced upon cooling is to be observed above and below this temperature interval. This may be clearly seen from the graphic representation of these changes in Figure 4. Below this temperature cooling is accompanied by a reverse rotation of the optic plane through its original position, while above the temperature the rotation upon cooling is in the same direction as that observed when heating the crystals.

Optical Changes in the Interval 192°-300° C

The difficulties of accurate observation increase rapidly as we pass to these higher temperatures. In the first part of this region, up to 250° C., the interference figures are clear and distinct, but the double refraction is so low that only a few of the leminiscate interference bands are visible. Above 250° C. observations can only be of a qualitative nature, because the optic axes soon pass out of the field of vision and any changes in the optical properties can be followed only by the movements of the few interference bands that remain visible. To these inherent difficulties are added the experimental difficulties of working at these temperatures.

At 300° C. the paraffine oil volatilizes rapidly and decomposition soon gives it a yellowish tint. Many of the poorer sections become opaque before this temperature is reached, because of the formation of a large number of small cracks through the crystal. These conditions tend to materially reduce the intensity of the light and the interference figures become hazy and indistinct. To take photographs of the interference figures, it is necessary to keep the lens systems in direct contact with the glass windows of the oil bath for twelve or fifteen minutes, so no photographs were taken above 192° C. because of the danger of cracking the lenses and of melting the canada balsam between the two sections of the nicol prism.

The changes which take place in the optical properties through this temperature interval may best be followed by referring to Figure 4, which shows the orientation of the optic plane and the size of the optic angle at different temperatures. From the photograph D, Figure 5, it may be seen that the double refraction is very low because there are no interference bands formed between the two optic axes. As the temperature increases, the size of the optic angle increases greatly but the double refraction still remains low.

Cooling from a temperature of 192° to 25° C. brings the optic plane into the position shown in photograph K, Figure 5a, in which the optic axes lie just outside the field of vision. If the crystals are heated to a higher temperature, the optic axes move still further outside of the field and none of the circular interference bands surrounding the optic axes are visible. Upon cooling from a temperature greater than 192° the plane of the optic axes always returns to the same position but the size of the optic angle changes slightly (Fig. 4).

The final stage is reached in the vicinity of 300° C. in which the position of the optic plane and the size of the optic angle do not vary upon heating and cooling. At this point the optic angle is greater than 90°; therefore, it is the obtuse bisectrix which is now perpendicular to the cleavage face (010).

DEHYDRATION AT CONSTANT TEMPERATURE

The resultant changes in the position of the optic plane and in the size of the optic angle, which are produced by heating to a definite temperature and allowing the crystals to cool in oil, are shown in Figure 4, A. to E. These changes are produced by dehydration and not by the influence of temperature; therefore it should be possible to duplicate these changes by dehydration with sulphuric acid. This was found to be the case.

If the crystals are placed in a desiccator over sulphuric acid they slowly dehydrate and an observable change in the position of the optic plane is produced in twenty-four hours. This method is very slow and the crystals become cloudy but their optical properties can be observed if they are immersed in oil. Heulandite is soluble in dilute acids but it is not attacked by concentrated sulphuric acid, so some of the crystals were placed in a small sulphuric acid bath and mounted between the polarizer and the analyzer. The strength of the acid was maintained by frequently removing it and replacing it with fresh acid.

Dehydration is comparatively rapid when the crystals are immersed directly in the acid and a noticeable change in the position of the optic plane takes place in fifteen minutes. The dehydration starts at the surface of the crystal and proceeds progressively inward with a consequent distortion of the interference figure, due to the fact that the crystal develops lamellae of different compositions. These anomalous figures are similar to those which develop when a crystal is rapidly heated in oil. Equilibrium is reached in two to three days and the resulting interference figure is similar to the photograph K, Figure 5a, except that the optic axes lie a trifle further outside the field of vision. The final rotation of the optic plane is the same as that produced by heating, although the increase in the size of the optic angle is not quite so pronounced. This indicates that the dehydration by the sulphuric acid was not quite so complete as that produced by heating.

This process of dehydration may be reversed by slowly diluting the acid. The addition of water to the sulphuric acid increases the vapor pressure of the acid and causes rehydration of the crystal. This rehydration can be carried to a point where the interference figure is similar to that shown in photograph J, Figure 5a. With further dilution of the acid the crystal rapidly disintegrates, due to the solvent effect of the dilute acid.

One crystal was mounted in a bath of absolute alcohol but no noticeable change was produced in twenty-four hours.

ROTATION OF THE OPTIC PLANE
(Values plotted in Figure 2

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
42° C.	2°	37° C.	2°	35° C.	2°15'
60	3	45	2 30'	38	2 15
65	4	47	3	42	3
$67\frac{1}{2}$	4 30'	55	4	45	3 30
$85\frac{1}{2}$	6 15	75	6 15	50	3 30
$94\frac{1}{2}$	7	$105\frac{1}{2}$	9 45	85	8
112	8 30	$122\frac{1}{2}$	12	$100\frac{1}{2}$	10
$116\frac{1}{2}$	10	$129\frac{1}{2}$	13	$110\frac{1}{2}$	10 30
133	12	158	17	$135\frac{1}{2}$	14 30
158	15 30	$165\frac{1}{2}$	18	144	16 30
177	18 30	177	20	163	19
185	22	192	33	177	21
192	27			192	35
202	44			212	67
212	62			218	73
224	79			$223\frac{1}{2}$	83
235	84			254	95
238	86			269	102
269	99				

ROTATION OF THE OPTIC PLANE UPON COOLING

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
85°	7°	110°	10°	120°	12°
72	3	92	5	102	$5\frac{1}{2}$
67	0	75	0	85	0
50	−1	64	−3	61	−6
45	−3	40	−7	40	−10
39	−4	25	−8	25	−11
25	−4				

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
137°	15°	150°	16°	161°	17°
105	1	130	9	121	3
50	−12	99	−2	75	−11
25	−14	83	−6	25	−21
		60	−12		
		41	−16		
		25	−18		

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
177°	20°	195°	36°	210°	59°
154	12½	160	58	200	63
141	7	139	67	155	80
121	−16	92	95	108	96
80	−22	60	106	85	104
25	−35	25	115	50	106
				25	112

| Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
229°	85°	260°	93°	300°	110°
186	87	200	94	100	113
160	87	130	98	25	112
130	94	110	103		
100	103	70	106		
50	110	25	117		
25	116				

STRUCTURAL CHANGES

No determinations of the lattice structure of the complex silicates have been made but Laue diagrams have been used to reveal the structural similarity of the silicates. Rinne[20] has also used the Laue diagrams to show the changes in symmetry which accompany dehydration of crystals and he gives diagrams of heulandite and meta-heulandite.

The photographs in Figure 6 were made upon the same crystals that were used for the determination of the optical properties, by alllowing the X-rays to strike perpendicularly upon cleavage sections parallel to (010). A is the Laue diagram of the normal heulandite at 25 ° C. B was taken upon the same section after it had been heated at 300°. C. for three minutes and allowed to cool in oil to room temperature. It shows no change in symmetry although the

[20] CRYSTALS AND THE FINE STRUCTURE OF MATTER, p. 146, (1924).

dehydration of the crystal has shifted the position of the optic plane from the horizontal until it is perpendicular to the two larger circles of the diagram. C was taken upon a section which had been heated at 210° C. for two hours and shows a slight breaking down of the structure though the main structural outlines still persist. In the photograph D we may see the decided change that has taken

Fig. 6.
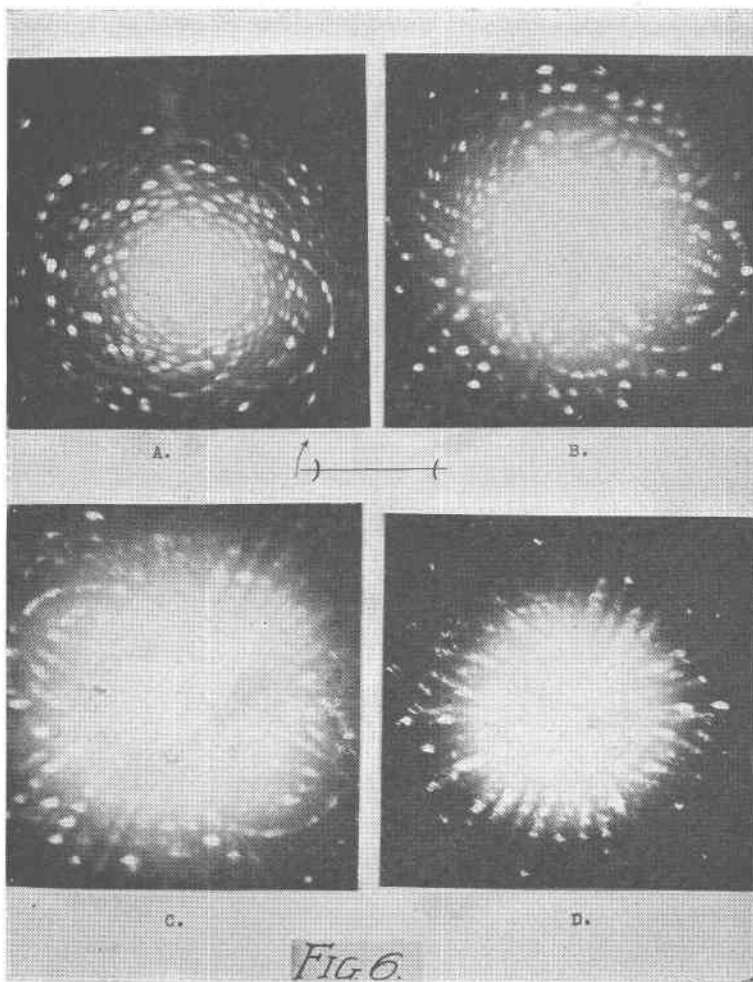
place in a crystal section which had been dehydrated in oil at 300° C two months previous to the time when the photograph was taken. This reproduction does not reveal the traces of the original structure as well as the negative, but the sunburst effect is characteristic of Laue diagrams of a heterogeneous mixture of minute crystals.

These diagrams indicate that meta-heulandite (Rinne) is a semi-permanent condition whose existence is dependent upon the stability of the silicate structure after the removal of the water. The gradual breaking down of this structure is revealed in the photograph D, Figure 6, which was taken two months after dehydration. Its similarity to the original structure is shown by B, Figure 6, taken immediately after dehydration. The structural significance of water in the silicates cannot be determined from X-ray studies because of the masking influence of the heavier elements.

DISCUSSION

From a consideration of the fact that the optical properties of heulandite bear a direct relationship to the amount of water present, we must conclude that the water is not extraneous, but plays a definite role in the structure of the crystals. If the water were present, not in any definite structural relationship but as an isotropic medium, its removal would have but slight effect upon the optical properties. If the water were present in its natural isotropic state and then were completely replaced by another isotropic substance (e.g., paraffine oil), the relative change in the double refraction would be about 1 per cent and would produce but a slight change in the interference figures. Such a hypotheses, then cannot account for the marked change that is observed when heulandite is dehydrated, and we must attribute this change to a structural alteration which is contingent upon the loss of water.

In dealing with the hydrated silicates, conditions are considerably different from those found in the typical hydrated salts. The amount of water present is much less and the tenacity of the crystal structure is much greater than in the hydrated salts. This is clearly shown in the following table. The values in the third column, the percentages of water by volume, are calculated from the first and second columns on the assumption (made for statistical comparsion only) that the water of the hydrate has a density of one.

	per cent H_2O(weight)	Sp. Gr.	per cent H_2O(volume)	Hardness
$Na_2SO_4.10H_2O$	55.9	1.48	82.7	1.5
$MgSO_4.7H_2O$	51.2	1.70	87.0	2.0
$FeSO_4.7H_2O$	45.3	1.89	85.6	2.0
$CuSO_4.5H_2O$	36.1	2.20	79.4	2.5
Heulandite	15.6	2.2	34.3	3.5–4.0
Chabazite	21.3	2.1	44.73	4.0–5.0
Apophyllite	16.1	2.3	37.03	4.5–5.0

In the hydrated salts the greater part of the crystal is water, and therefore, the crystal form would be dependent to a great extent upon the H_2O molecule. The loss of this water would necessarily destroy the crystal form. On the other hand, in the hydrated silicates, water plays a minor rôle and the crystal form would be determined by the silicate molecule. This hypothesis may account for the stability of the crystal form of zeolites after losing the water of crystallization. Added evidence of the stability of the crystal structure of the two types of hydrates may be found in the comparative hardness. Mohs's scale of hardness is only a relative standard but determinations of absolute difference in hardness between 2 and 4, as given in Mohs's, range as high as 1 to 20.

The existence of water in a definite structural relationship to the silicate molecule will account for the variations in the optical properties that have been observed in the crystals of heulandite. The gradual removal of this water, by heating slowly to 177° C. would produce a change in the fields of force surrounding the silicate molecule and consequently a change in the optical properties. Above a temperature of 177° C. the cumulative effect of these stresses would be so great that they would produce a rupture in the silicate structure which is revealed in both the optical changes and in the Laue diagrams. The final and complete breaking down of the crystalline structure is very slow and must be measured in periods of months duration.

SUMMARY

1.   Water plays a definite role in the structure of heulandite.

2.   Above a temperature of 177° C. the structure of heulandite exists in a metastable condition. This is the metaheulandite which Rinne has established from Laue diagrams, but its persistence is due to the stability of the silicate structure and will break down if given a long enough period of time. The development of this

metastable condition is correlated with the 3 molecule hydrate (Weigel and Scheuman).

3. The optical variations shown in Figure 4, A to E, are due to dehydration alone while the more pronounced changes are due to temperature effects.

4. The crystals always remain biaxial and positive. The apparent uniaxiality is due to the rotation of the optic plane when the angle of the optic axes is small.

5. During all the changes observed, the bisectrix remains parallel to the *b* axis, which indicates that the crystals are monoclinic.