# PROPERTIES OF ROCHELLE SALT RELATED TO THE PIEZO-ELECTRIC EFFECT.

By Joseph Valasek.

## Synopsis.

*Temperature variation of several physical properties of Rochelle salt, from* $-30°$ *to* $+30°$ *C.*, was undertaken to determine which of them seem to be related to the piezo-electric effect, which increases rapidly between $-20$ and $-15°$ C. and decreases rapidly between $+20$ and $+30°$ C. In this way it was hoped to get information as to the nature of the structure underlying piezo-electric phenomena. *Refractive indices* were measured for the three principal directions for six wave-lengths from 4554 to 6500 Å. and at temperatures of $-70$, $-11.5$, 0, $+21.3$ and $+40°$ C. The variation with temperature, however, is linear, the average coefficient being $59 \times 10^{-6}$ per degree. The *thermal expansion* between $-10$ and $+20°$ C. was measured by the Fizeau method for the three principal directions. The ratio of $(n^2 - 1)$ to $\rho$ is approximately constant, in agreement with the Sellmeir formula for dispersion, and if the change in refractivity is regarded as due to the change in density, reasonable values are obtained for the constants in the Lorentz formula. The *specific rotatory power of an aqueous solution* of the salt was found to change less than 0.4° in the interval from $+4$ to 40° C., giving no indication of a change in molecular asymmetry in this interval. The value obtained at 25° C. is 25.9° for sodium light, lying between the results of previous observers. The *electrical conductivity* increases only from $2 \times 10^{-14}$ mhos/cm.$^3$ at $-65°$ C. to $5.4 \times 10^{-14}$ at $-20°$ C. Between $-20°$ and $+30°$ C., however, it was found to depend on the direction of the current, being only half as great in one direction as in the other at 0° and at 20°; and above 20° it increases very rapidly to $5 \times 10^{-9}$ at 43°. At all temperatures, however, the current was found proportional to the applied field, at least up to 10,000 volts/cm. *The reversible electro-optic rotation* was observed in the direction of the field, using transparent alcohol electrodes and plane polarized light of wave-length 5737 Å. At 20° the rotation of the $\alpha$ and $\beta$ axes in their plane per unit field normal to them is $1.7 \times 10^{-4}$ degrees, and decreases for higher temperatures much as the dielectric constant does. The electro-optic constant $e_{41}$ was also computed. Although Rochelle is classed as a type of crystal that should show no *pyro-electric effect*, a "real" effect was observed in the ă crystallographic direction as the crystal was gradually heated at a constant rate. The coefficient changes sign just below room temperature and becomes very large.

*Theory of piezo-electricity is discussed* briefly in the light of these results. In view of the fact that none of the properties measured show changes with temperature which correspond with those of the piezo-electric effect it is probable that the elastic or piezo-optic constants must change in such a way as to account for the piezo-electric changes.

*Newman's Principle of Symmetry in Crystal Optics.*—Rochelle salt, if it belongs to the hemihedral class of the orthorhombic system, seems to form an *exception* to this principle since most of its electrical properties in the direction of the ă axis depend on the direction of the field.

*Infra-red absorption band for Rochelle salt* is computed from the constants of the dispersion formula to be at about 55 $\mu$.

THE experiments herein described were initiated for the purpose of examining some of the properties of Rochelle salt which might be related to the piezo-electric property and thus to obtain further information on the nature of the structure underlying piezo-electric phenomena. Rochelle salt is particularly suited for this study because its piezo-electric reaction is relatively large and because of the marked changes which occur in its activity at certain temperatures. As the crystal is heated from low temperatures, there is a sudden increase in activity between − 20 and − 15° C. and a corresponding decrease between + 20 and + 30° C. as the following table shows. The piezo-electric modulus given here is defined as the electric polarization in the ă crystallographic direction per unit shear in the plane normal to it.

TABLE I.

| Temperature. | Piez. Modulus. |
|---|---|
| − 70° C. | $0.017 \times 10^{-5}$ |
| − 50 | 0.017 |
| − 30 | 0.065 |
| − 20 | 1.08 |
| − 10 | 6.07 |
| 0 | 6.75 |
| + 10 | 7.42 |
| + 20 | 8.10 |
| + 30 | 1.08 |
| + 40 | 0.41 |

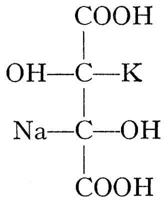
In those temperature intervals where the piezo-electric property makes rapid changes, the writer has undertaken to study various other physical properties of the crystal. In the first place the variation with temperature was studied with the thought that the same type of structure may be responsible for both the piezo-electric property and the optical rotation or that they may be related in some way. Then again measurements were made on the indices of refraction because a shift in an absorption band caused by a changing restoring force of the ions producing the piezo-electric effect would be reflected in the indices of refraction if the absorption bands involved were not too far away from the visible region. Furthermore, observations were made on the reversible electro-optic effect.

We shall begin by reviewing some general facts concerning Rochelle salt. This substance is a double tartrate of sodium and potassium with the chemical formula $NaKC_4H_4O_6 \cdot 4H_2O$. It crystallizes in the orthorhombic system, showing sphenoidal hemihedrism. It is optically active both as a crystal and in solution. It is, of course biaxial, as the crystal

---

[1] Valasek, PHYS. REV., XIX., 478, 1922.

system shows. The structural formula is



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{OH—C—K} \\ | \\ \mathrm{Na—C—OH} \\ | \\ \mathrm{COOH} \end{array}$$

This form has the usual type of asymmetry occurring in optically active carbon compounds. The crystal is brittle and soluble in water. This latter property enables one to cut it by a wet string running over pulleys and through water, and to polish it on a slightly moistened piece of ground glass. Since it cracks very easily due to unequal or too rapid temperature changes, it must be handled carefully. It cannot be heated above 53° C. as it transforms here into water and the single tartrates of sodium and potassium with an absorption of heat. A moderately sensitive differential thermocouple scheme indicates no sharp heat transformation anywhere between $-70$ and $+54°$ C. On heating, however, there begins a slow and steady apparent heat evolution at 24° C. which continues up to 53° C. This is thought to be due to either an increase in thermal conductivity or to a steadily decreasing specific heat.

## Refractivity.

The three principal indices of refraction were determined by a prism and spectrometer method for a number of wave-lengths. For measurement at various temperatures the crystal was mounted on a pedestal about ten centimeters high so as to be in the center of the double-walled vessel which contained the heating or cooling mixture. A cross-section of this arrangement is shown in Fig. 1*A*. Tubes *A* and *B* (1 x 2 cm.) served as passages for the light between the collimator and the telescope. Diaphragms *C* and *D* together with end plugs and plane-parallel windows served to cut down air circulation. The copper-constantan thermocouple which measured the temperature came up to the crystal through the hollow pedestal, which was largely made of thin-walled glass tubing. The cold junctions were kept in ice and the electromotive force was measured by a Leeds and Northrup Type K potentiometer. The thermocouple was calibrated at the fixed points given by fresh liquid air, frozen mercury, ice, and steam.

The prism used was cut from a large crystal about five centimeters along each edge, in such a way that one of the faces was a natural crystal face while the other was nearly parallel to the b and c crystallographic axes (Fig. 1*B*). In order to procure faces as flat as possible, a large prism was first cut and polished. From its center was cut the small prism about 2 cm.$^3$, which was used in the experiments. Diaphragms of black paper served to still farther cut down the areas of the faces, care being taken not to decrease the resolving power so much as to cause a noticeable lack of precision in setting on the spectrum lines. In this way a good double spectrum was obtained from which two indices could be determined. These indices will be denoted by $n_1$ and $n_2$ in the order of their magnitude.

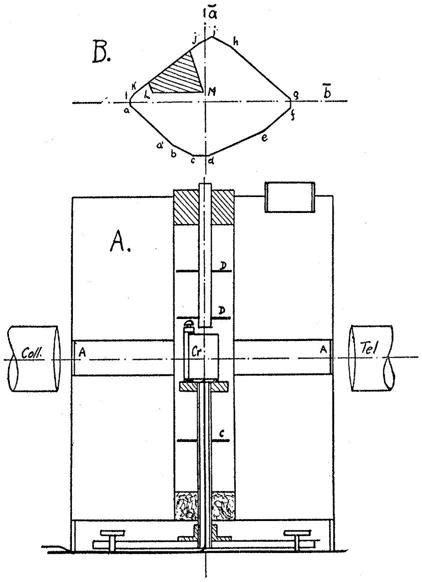


Fig. 1.

Mounting of prism for refractivity measurement.

The source of light was an arc between carbons containing barium chloride. This source gives a set of six bright lines fairly well distributed throughout the spectrum and proved to be very convenient for the determination of dispersion.

In calculating the three main indices, Fresnel's formulæ for inactive crystals were used in spite of the fact that Rochelle salt is active.[1] This is permissible in this case because the indices were not measured closer than five units in the fifth decimal place and because the rotatory power of the crystal produced much smaller deviations from Fresnel's formulæ. Following Pockel's *Krystalloptik*, $\alpha$, $\beta$, and $\gamma$ will be used to denote the three main indices in the order of increasing magnitude and $\nu_1$, $\nu_2$, and $\nu_3$ to denote the direction cosines of the wave normal in the crystal with respect to the principal axes. The indices $n_1$ and $n_2$ in an equatorial plane $\nu_1 = 0$, that is, normal to the $\alpha$ axis of the index-ellipsoid, will be given by the two $n$ roots of the equation:

$$\left\{\frac{1}{\alpha^2} - \frac{1}{n^2}\right\}\left\{\left(\frac{1}{\gamma^2} - \frac{1}{n^2}\right)\nu_2^2 + \left(\frac{1}{\beta^2} - \frac{1}{n^2}\right)\nu_3^2\right\} = 0. \qquad (1)$$

In this plane, one of the indices, namely $n_1 = \alpha$, should be the same in all directions. This was found to be accurately true and is taken to justify our use of the simpler formula.

The orientation of the crystal was roughly as shown in Fig. 1 *B*, the

---

[1] Pockels, Krystalloptik, 31.

LM face being normal to the ă axis within three degrees as determined from the crystal angles. The middle and greatest indices were calculated from formula (1) by solving for $\beta$ and $\gamma$ when measurements of $n_2$ had been made for two known directions. The value of $\beta$ so found differed by only 0.00002 from the value of $n_2$ normal to the face LM. The two directions chosen were normal to the faces of the prism.

The crystal was clamped in place by the edge facing the collimator so that when its angle changed due to anisotropic expansion[1] the light would still be normally incident on this face. If the constants for the two directions are respectively unprimed and primed, the following set of formulæ give the indices:

$$\begin{aligned} n_1 &= \frac{\sin A_1}{\sin(A_1 + D_1)}, \quad \text{etc.,} \\ \alpha &= n_1 = n_1', \\ \beta^2 &= \left(\frac{\nu_3}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2' - \left(\frac{\nu_3'}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2, \qquad (2) \\ \gamma^2 &= \left(\frac{\nu_2}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2' - \left(\frac{\nu_2'}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2. \end{aligned}$$

The angles of the prism $A$ and the angles of deviation $D$ were measured on the spectrometer by standard methods at a number of steady temperatures between − 70 and + 40° C. A nicol prism was used in front of the eyepiece to keep the two spectra distinct.

A set of careful determinations of the three indices was made in this way for the six lines of the barium spectrum at room temperature with the windows of the cooling chamber removed. These are given in Table II.

### Table II.

*Temperature 21.3° C.*

| Wave-length. | $\alpha$. | $\beta$. | $\gamma$. |
|---|---|---|---|
| 4554.2 Å | 1.49906 | 1.50062 | 1.50504 |
| 4934.2 | 1.49565 | 1.49734 | 1.50154 |
| 5535.7 | 1.49170 | 1.49348 | 1.49721 |
| 5853.9 | 1.49001 | 1.49183 | 1.49540 |
| 6141.9 | 1.48878 | 1.49056 | 1.49430 |
| 6497.1 | 1.48743 | 1.48920 | 1.49280 |

The directions of the $\alpha$, $\beta$, and $\gamma$ axes of the index ellipsoid are respectively the same as the directions of the c, $\bar{\text{b}}$, and ă crystallographic axes.

Above and below room temperature, coverglasses cemented on with

---

[1] Voigt, Krystallphysik, 276.

Canada balsam had to be applied to preserve the polish of the prism. With the apparatus entirely assembled another set of determinations was made at the same temperature and corrections found for the cover-glasses and windows. The indices were then measured for steady temperatures of − 70, − 11.5, 0.0, + 21.3, and + 40° C. The angle of the prism at these temperatures was measured by a reflecting eyepiece.

The main indices were calculated and plotted and it was observed that their variation with temperature was practically linear. From the best set of straight lines through the points the following values were obtained for the indices at 0° C. and for the temperature coefficients.

TABLE III.

| Wave-length. | Indices at 0° C. | Temp. Coefficient. |
|---|---|---|
| 4554.2 | 1.5004 | 0.000064 |
| | 1.5019 | 58 |
| | 1.5063 | 68 |
| 4934.2 | 1.4970 | 63 |
| | 1.4987 | 58 |
| | 1.5029 | 65 |
| 5535.7 | 1.4930 | 64 |
| | 1.4947 | 58 |
| | 1.4986 | 63 |
| 5853.9 | 1.4913 | 61 |
| | 1.4930 | 60 |
| | 1.4968 | 58 |
| 6141.9 | 1.4900 | 61 |
| | 1.4917 | 58 |
| | 1.4953 | 61 |
| 6497.1 | 1.4888 | 63 |
| | 1.4905 | 59 |
| | 1.4939 | 59 |

The values of $\alpha$ and $\beta$ in both tables are more accurate than those of $\gamma$ because the latter are obtained by solving the equation of the oval for its major axis which is respectively about 90° and 40° from the directions of the radii measured. In Table II. the values of $\alpha$ and $\beta$ are good to $\pm 0.00005$, while $\gamma$ is good to $\pm 0.00015$. The values in Table III. may be in error by greater amounts because of the greater variety of chances for error that present themselves in measurements at other than room temperature.

A surprising outcome of these measurements is that there is no marked change in optical properties between − 70 and + 40° C. This was contrary to expectation and shows that there is no gross change in crystal structure occurring between these temperatures. This eliminates one explanation that may be advanced for the variation in piezo-electric response that occurs in this range.

Drude's dispersion theory applied to this data gives a little information as to the nature of the bound charges. The best set of observations for this purpose is the $\alpha$ set given in Table II. since it is checked by a greater number of independent observations and is a directly measured result. Suppose we take the five-constant formula:[1]

$$n^2 = -B'\lambda^4 - A'\lambda^2 + A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \tag{3}$$

According to the theory the constants should all be positive and respectively given by the formulæ:

$$\begin{gathered} B' = \sum\frac{\Theta_r}{\lambda_r^2}; \qquad A' = \sum\frac{\Theta_r}{\lambda_r^4}; \\ A = 1 + \sum\Theta_v; \qquad B = \sum\Theta_v\lambda_v^2; \qquad C = \sum\Theta_v\lambda_v^4, \end{gathered} \tag{4}$$

where the subscript $r$ means that the summation is to be carried out only for charges whose free period lies in the infra-red, while $v$ refers in a similar fashion to the ultraviolet charges, and $\Theta$ is the contribution of each type to the dielectric constant. If there is only one predominating type of each, the summation signs can be removed and we have

$$\lambda_r^2 = \frac{K - A}{A'}, \tag{5}$$

where $K$ is the ordinary dielectric constant and

$$K = 1 + \sum\Theta_v + \sum\Theta_r = A + \sum\Theta_r. \tag{6}$$

Evaluating the constants of (3), it is found that

$$\begin{aligned} B' &= -0.163, \\ A' &= +0.215, \\ A &= +2.282, \\ B &= -0.007, \\ C &= +0.002. \end{aligned}$$

Since $K$ has the value 645 at 20° C., it is found that the infra-red absorption band should be at 55 microns.

---

[1] Drude, Optik,

Inspection of the values above shows that the constants $B$ and $B'$ have the opposite sign to that which the theory gives. The observations are considered to be fairly reliable as measurements on several crystals show, so that the sign is not due to error.

In a previous paper the writer has calculated the position of an absorption band from piezo-electric data.[1] The expression used was derived on the assumption that $\alpha = 1/3$, where this $\alpha$ is defined by the relation $E = E_p + \alpha P$, and $E_p$ is the field at a charge in a medium whose polarization is $P$. It will be shown in the following that $\alpha$ is far from 1/3 for Rochelle salt, but that this constant can be eliminated anyway. The equation for the $X$ component of vibration of an ion of charge $e$ and mass $m$ is:

$$m\ddot{\xi} = eX - 4\pi e^2\left(\frac{1}{\theta} - \alpha N\right)\xi. \tag{7}$$

The wave-length of the free vibration is then

$$\lambda = \left\{\frac{c^2\pi m}{e^2}\left(\frac{\theta}{1 - \alpha N\theta}\right)\right\}^{1/2}. \tag{8}$$

If the contribution of this ion to the dielectric constant is $K_r$ and there are $N$ such ions per cubic centimeter, then

$$K_r = 1 + \frac{N\theta}{1 - \alpha N\theta} \tag{9}$$

and we have

$$\lambda = \left\{\frac{c^2\pi m(K_r - 1)}{Ne^2}\right\}^{1/2}, \tag{10}$$

which is independent of $\alpha$ but contains $K_r$. Since this is very nearly equal to the entire dielectric constant between − 20 and + 20° C., we shall replace $K_r$ by $K$. The difference between these two quantities is the constant $A$ of the dispersion formula and $K$ is well in the hundreds at these temperatures. The quantities $N$, $m$, and $e$ are unknown, but it should be interesting to try some possible values. For convenience let us rewrite the expression by putting $S$ equal to the sum of the atomic weights of the atoms in this ion, letting $\sigma$ be the sum of the chemical valencies, and $u$ be the number of such ions in each molecule. Then we have:

$$\lambda_r = 0.741\sqrt{\frac{(K - 1)S}{\sigma^2 u}}. \tag{11}$$

Since the infra-red ions are always of atomic or molecular magnitudes

---

[1] PHYS. REV., XIX., 489.

and because the water of crystallization is so important to the piezoelectric properties, it may be that either the O or the OH ion is the important one. Taking the value of $K$ as 645 at 20° C., it is found that the natural wave-length for the two cases above is respectively 9.5 and 40. The latter gives the better agreement with the value found from the dispersion theory. It must be admitted that there are many arbitrary assumptions in the above. This, however, is as much as can be done at present.

The temperature coefficients of the indices given in Table III. turned out to be relatively large. This would ordinarily mean that the coefficient of volume expansion is large. On either Drude's or Lorentz's dispersion theory, the variation in the indices of refraction of any single chemical compound should be dependent entirely on the variations in the numbers of dispersion charges per unit volume. This number varies inversely as the density. The Lorentzian relation[1] between index of refraction $n$ and density $\rho$ may be written in the following form:

$$\frac{1}{\rho} = \frac{C}{n^2 - 1} + C\alpha, \tag{12}$$

where

$$C = \frac{1}{\rho}\sum \frac{v_s^2 e_s^2}{m_s(p_s^2 - p^2)}. \tag{13}$$

Knowing $n$ and $\rho$ at various temperatures enables one to find the constants $C$ and $\alpha$ and to test the theory.

## Thermal Expansion.

To find the variation in specific volume with temperature, the coefficients of linear expansion were measured in the three principal directions by the Fizeau method.[2] A plan of the apparatus is shown in Fig. 2. The three tripods which supported the optical surfaces were made of iron so as to expand very much less than the crystal. A thermocouple T.C., whose junction nearly touched the crystal, was used to measure the temperature. The movement of the rings between two steady temperatures was observed in the telescope Tel. The apparatus had to be sealed to exclude moisture; otherwise this would condense on the small tripod points $p$ and cause them to sink in. The way this occurred is interesting. The inset in Fig. 2 shows a cross-section of one of the pits.

In each of the crystallographic directions a set of measurements of the relative expansion of crystal and apparatus was made for the temperature

---

[1] Richardson, Electron Theory, p. 148.

[2] Tutton, Crystallography, p. 884.

interval of − 10 and + 20° C. using a cube of Rochelle salt. The dimensions of the cube were: 1.302 × 1.271 × 1.163 cm. and its faces were cut and polished within 3° of normal to the crystallographic axes. The expansion of the apparatus was measured by using a cube of lead whose coefficient was taken to be 0.00002726. This cube was cut from a Bureau of Standards melting point sample and was nearly pure. The average coefficients of expansion between − 10 and + 20° C. for Rochelle salt were thus found to have the values:

$$a = 0.0000599 \pm 4,$$
$$b = 0.0000381,$$
$$c = 0.0000448.$$

The coefficient of volume expansion is accordingly:

$$\Delta = 0.0001428.$$

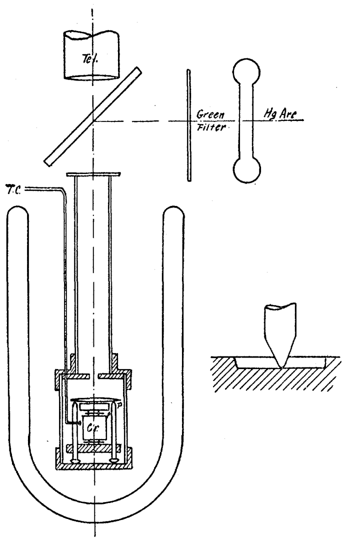


Fig. 2.
Dilatometer.

Since the density of Rochelle salt at 0° C. was found to be 1.766 we have for any other temperature; $\theta$°C:

$$\delta = 1.766 - 0.0002522\,\theta.$$

As noted above these values are the averages over a temperature range of thirty degrees extending from − 10 to + 20° C. Lower temperatures could not be conveniently kept steady for a long enough period of time, while at higher temperatures there was trouble due to condensation of traces of moisture on the crystal as soon as the surroundings were warmed. Unless the end temperatures were steady for about half an hour one could not obtain very reliable results as it took that long to be sure that the fringes were perfectly steady. It was desirable, however, to see if a change in dimensions could be detected at − 20° C. where the crystal became active. Observation of the movement of the fringes during a slow and uniform rate of heating of 2° per minute from the temperature of carbon-dioxide snow gave a smooth curve for all three crystallographic directions. There can be no abnormal change in dimensions comparable with the wave-length of mercury-green light unless this is spread out over a range of about ten degrees or more.

According to the Lorentz formula (12) there is a linear relation between

$1/\rho$ and $1/(n^2 - 1)$. This gives a set of three straight lines for any one wave-length, whose slopes are $C_1$, $C_2$, and $C_3$, and whose $y$ intercepts are $C_1\alpha_1$, $C_2\alpha_2$, $C_3\alpha_3$. The values of $\alpha$ are of interest as bearing on the effect of surrounding polarization on the dispersion charges. For a cubical arrangement of charges it is found to be equal to one third. Drude, in his dispersion theory, assumes that the force on the dispersion charges is equal to the electric vector of the incident wave times the charge, that is, he puts $\alpha$ equal to zero. This theory leads to the Sellmeier type of formula. Lorentz's formula differs from this only in so far as no assumptions have been made regarding the value of $\alpha$.

The values of $C$ and $\alpha$ given by the best straight lines through the calculated points are as follows:

Table IV.

| Wave-length. | $C$. | $\frac{n^2 - 1}{\rho}$. | $\alpha$. |
|---|---|---|---|
| | 0.706 | 0.716 | 0.003 |
| 4554.2 | 0.729 | 0.710 | 0.080 |
| | 0.660 | 0.707 | 0.068 |
| | 0.660 | 0.705 | 0.043 |
| 5535.7 | 0.718 | 0.698 | 0.078 |
| | 0.657 | 0.695 | 0.043 |
| | 0.648 | 0.696 | 0.041 |
| 6497.1 | 0.673 | 0.690 | 0.021 |
| | 0.683 | 0.689 | 0.017 |

The values of $\alpha$ are evidently much nearer zero than one third and the dispersion should be fitted fairly well by Sellmeier's formula. The values of $C$ roughly agree with $(n^2 - 1)/\rho$ as the table shows. This agreement should be perfect when $\alpha$ is zero.

The values of $C$ and $\alpha$ above are calculated so that the variation of the index of refraction with temperature is accurately accounted for by the dilatation of the crystal. Since their values are not unreasonable, at least the bulk of the change in indices can be so accounted for.

The variation in $C$ must be all due to changes in the natural period $p_s$ for any one color. The above values show that the absorption bands for the three principal indices are substantially the same in the infra-red but may differ in the ultraviolet. The small $\alpha$ means that the force on a unit charge per unit polarization is small, just as though the charge were well shielded.

## OPTICAL ACTIVITY.

Since the optical activity and piezo-electric property always occur simultaneously in crystals having an asymmetric structure, it was decided to study the optical activity of Rochelle salt. Substances forming such crystals may be rotatory when dissolved or melted, like Rochelle salt and sugar, or they may be only active in the crystalline state, like quartz. If they are active in the non-crystalline condition, it is due to an asymmetric molecular structure. Such substances are as a rule carbon compounds and the asymmetry may be pictured by a structural formula in space in which the four radicals combined with the carbon atom are placed at the corners of a tetrahedron. J. J. Thomson[1] has shown that in the case of active solutions the molecules must have both dynamic and electric asymmetry, while in a crystal either type is sufficient to produce activity.

There is reason to believe that the piezo-electric property is rather due to inter-molecular reactions in the crystal structure, so that naturally, it would be best to measure the rotatory power of the crystal in the directions of the optic axes. This has been done at ordinary temperatures by Pocklington[2] and is the first such determination for a biaxial crystal. He found that the plane of polarization of sodium light was rotated − 1.2° per millimeter in the directions of both binormals. This work was repeated and extended to other crystals by Dufet, who found for Rochelle salt − 1.35 instead of − 1.2. There is difficulty in carrying out such measurements at different temperatures because of the movement of the optic axes.

The rotatory power of the solution can, however, be measured without much difficulty, but the range of temperatures is very limited and covers only that one of the critical points which is at room temperature. At any rate some alteration in molecular structure may be detected here. One may suppose, moreover, that a change in molecular structure would be the basis of any change in crystal structure.

Observations were accordingly made on the rotation by a solution of a crystal of Rochelle salt in water. A ten-centimeter polarimeter tube was inserted in a double-walled chamber which could be filled with water and heated electrically. The temperature was measured by a copper-constantan thermocouple whose junction was tied to the center of the polarimeter tube. The brass ends of the tube were coated by a thin film of paraffin to keep the solution from attacking them and becoming contaminated.

---

[1] J. J. Thomson, Phil. Mag., Dec., 1920.

[2] Pocklington, Phil. Mag. (6), II., 368, 1901.

The concentration of the solution was determined by evaporating a carefully weighed portion in a hot water bath and then drying the residue under a bell-jar with $P_2O_5$ in vacuo until the weight showed no further diminution. The remainder was assumed to be the anhydrous salt. The concentration used was 0.264 grams of the anhydrous salt per cubic centimeter of solution at 4° C. The density of the solution decreases by about a half per cent. between 4 and 30° C. Effects of expansion of the polarimeter tube are negligible.

The specific rotations for sodium light are shown plotted against temperature in Fig. 3.

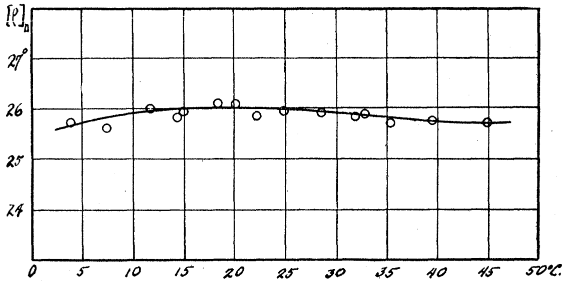


Fig. 3.

There seems to be a considerable lack of agreement between values given by various investigators for the rotatory power of Rochelle salt solution and the present value does not agree with any of them. In Dufet's tables the following figures are given:

| $[\rho]_D$ | Concentration. | Authority. |
|---|---|---|
| 22.42....... | $c = 20$ hydr. | Krecke, 1872. |
| 29.67....... | $c = 10.77$ anh. | Landolt. |
| 29.5........ | $c = 21.0$ anh. | Kummel, 1891. |
| 29.53....... | $c = 9$ to 43 anh. | Thomsen, 1886. |
| 22.12....... | $c = 5$ to 45 anh. | Long, 1888. |

The concentration is given in grams per one hundred cubic centimeters of solution. The present value comes just between the two extremes.

The differences can hardly be due to error in measuring the rotation so that it seems that they must be due to differences in taking care of the water of crystallization in calculating the concentration, or possibly due to a very impure salt. The writer has also checked his result by measuring the rotation by a weighed amount of hydrated Rochelle salt in a weighed amount of water. The weight of the water of crystallization was calculated from molecular weights and subtracted from that of the salt and added to that of the water. Using the density of water the grams of anhydrous salt in a cubic centimeter of solution was found. The final results were 26.4 and 25.8 on two different trials.

In conclusion, however uncertain the value of $[\rho]$ is, it is at least evident that no marked change in rotatory power occurs at 20° C. The molecular structure which accounts for optical rotation is therefore independent of the piezo-electric structure.

## ELECTRICAL CONDUCTIVITY.

In a recent paper the writer has reported a variation in electrical conductivity of Rochelle salt with temperature.[1] It appeared that there was a very marked and continuous increase in conductivity beginning at 23° C. when the crystal was heated at a uniform rate from the temperature of carbon-dioxide snow. Under normal conditions the crystal was about as good an insulator as ordinary glass when the surfaces were dry and the temperature was less than 23° C. There has been recently reported [2] an increase in conductivity for alternating currents even at temperatures below 23° C. when the field exceeds about 3,500 volts per centimeter. In view of this it seemed advisable to extend the writer's work on conductivity for direct currents by making measurements for various applied fields at different temperatures.

The conductivity was determined by measuring the current through the crystal by a sensitive galvanometer and the voltage across it by an electrostatic voltmeter. The galvanometer was of 650 ohms resistance and was shunted by 20,000 ohms so as to be nearly aperiodic. Its sensitivity under this condition was $1.108 \times 10^{-9}$ amperes per millimeter deflection.

The direct electromotive force was furnished by a transformer giving up to 10,000 volts in connection with a rectifier. A Coolidge tube proved convenient for rectification since the current was only enough to take care of insulation leakage. The diagram of connections is shown in the figure below. The battery of Leyden jars across the terminals was of sufficient capacity to keep the system charged for several seconds after the transformer was cut off.

The leads were soldered to the tinfoil plates which were cemented to the crystal with shellac. To one of the plates there was also soldered a copper-constantan thermocouple to measure the temperature of the crystal. To help reduce errors due to surface leakage, the tinfoil plates did not extend closer than two millimeters from the edges of the plate.

---

[1] PHYS. REV., XIX., p. 488.

[2] J. G. Frayne, Wash. Meet. of Am. Phys. Soc., April, 1922.

The surfaces were dried by phosphorus pentoxide and then coated with paraffin. The sample so prepared was suspended by the leads in the center of a large glass test tube. The wires were sealed through glass tubes which passed through the stopper. Diaphragms, wool plugs, and a brass cylinder helped to keep the temperature uniform. The tube containing the crystal was cooled by cold packs or baths or heated by the electric heater which surrounded it.

It was soon realized that when the applied potential became too great there was a corona discharge off the edges of the tinfoil. The first noticeable increase in conductivity due to this cause came at about 12,000 volts per centimeter through the crystal. There is reason to believe that the apparent increase in conductivity for alternating fields in the work referred to above is due to corona unless special precautions were taken to eliminate it. Experiments show that the corona loss may start at much lower potentials if the electrode edges are not separated or protected in some way.

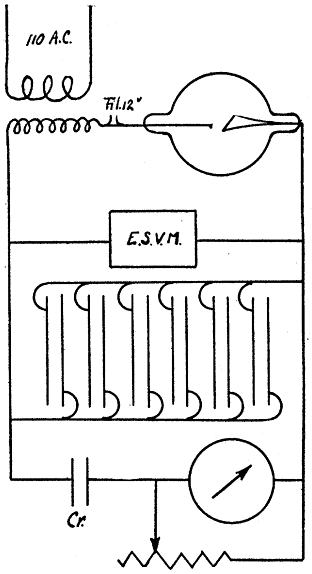


Fig. 4.

For Rochelle salt it was found that no marked increase in conductivity or other deviation from Ohm's law occurs below 10,000 volts per centimeter and probably none below double that field.

The conductivity was found to depend on the direction of the current for some temperatures. This occurred in the range of maximum piezoelectric activity, the greater conductivity being in the direction, (+), of the permanent polarization.[1] Even in this case the relation of current to field was linear within the above field limits.

Table IV.

| Temperature. | Conductivity. |
|---|---|
| − 65° C. | 2.0 × $10^{-14}$ mhos/cm.$^3$ |
| − 40 | 3.6 × $10^{-14}$ |
| − 20 | 5.4 × $10^{-14}$ |
| 0 | + 9.0 × $10^{-14}$ and − 5.0 × $10^{-14}$ |
| + 20 | + 22.0 × $10^{-14}$ and − 11.0 × $10^{-14}$ |
| + 30 | + 11.8 × $10^{-13}$ and − 11.1 × $10^{-13}$ |
| + 35 | 1.00 × $10^{-11}$ |
| + 43 | 5.00 × $10^{-9}$ |

---

[1] Phys. Rev., XVII., p. 476.

Values at higher temperatures will be found in one of the writer's papers.[1]

In the paper just referred to, it was reported that the crystal begins to conduct at 23° C. What was really meant was that conduction below this temperature seemed negligible. This, of course, depends on the sensitivity of the instruments used and on the scale in plotting curves. By changing these, apparently sharp bends in exponentially increasing curves may be put nearly anywhere. As the above table shows, there are no sharp breaks in the conductivity curve.

It is interesting that the conductivity is different for currents in opposite directions in the temperature range where the crystal is piezo-electrically active. The significance of this is not fully understood but it seems to be connected with the permanent polarization and related polar effects as will be pointed out in the concluding discussion. If the polarization were not so small, this would be in accordance with Thomson's theory of conduction, the essential feature of which is the shooting of electrons from atom to atom by a sort of radio-activity induced by the field.

## ELECTRO-OPTIC EFFECT.

The reversible electro-optic effect in acentric crystals has been studied for several substances, including Rochelle salt, by F. Pockels.[2] These types of crystal are always piezo-electric and exhibit an electro-optic effect analogous to the Kerr effect except that the polarization constants vary in a linear manner with the field instead of the square. Pockels' observations have considerable theoretical interest because he was able to show that the effect is only partly due to the mechanical action of the electric field and that there is a part due to a direct influence of the applied field on the vibrations of the charges in the medium. This change in the periods, which is analogous to the Stark effect, affects the optical properties of the substance.

To completely determine any general variation in the optical properties of a crystal, the positions and magnitudes of the three main indices must be fixed. This may be done by six quantities called polarization constants or optical parameters.[3] Pockels develops a set of formulæ by first writing the most general expression for each of these parameters in the form of a power series in ascending powers of either the field or the polarization. The reversible electro-optic effect must be expressible in odd powers alone, and for fields not too great, this may be taken as the first. This effect is observed in all acentric crystals and in no other

---

[1] PHYS. REV., XIX., p. 488.

[2] Pockels, Krystalloptik, p. 492, and Voigt, Magneto- u. Elektro-optik, p. 341.

[3] Pockels, Krystalloptik, p. 66.

types. The irreversible or Kerr effect must be an even function of the field and as a first approximation, the first may be taken. This effect is observed in all substances but needs a relatively greater field to bring it into prominence. These general formulæ are then simplified by considering the symmetry of the particular crystal system to which they are to be applied. This is done by adjusting the coefficients so as to put the equations into such a form that transformations of the axes into physically equivalent positions keeps their form invariant. These physically identical positions are found by a consideration of crystal symmetry which is their most general manifestation. The equations for the hemihedral class of the orthorhombic system are:

$$\begin{aligned} a_{11} &= a_0^2; & a_{22} &= b_0^2; & a_{33} &= c_0^2. \\ a_{23} &= e_{41}P_x; & a_{31} &= e_{52}P_y; & a_{12} &= e_{63}P_z. \end{aligned} \tag{15}$$

In these equations $a_{11}$, etc., are the six polarization constants; $a_0$, $b_0$, $c_0$ are the initial values of the principal wave-velocities; $P_x$, $P_y$, and $P_z$ are the components of the polarization, which is assumed to be a linear function of the field, and $e_{41}$, $e_{52}$, and $e_{63}$ are the three remaining constants which describe the electro-optic behavior of this class. These formulæ show that since the first three parameters do not change, the only effect in this type of crystal is the rotation of the principal axes around the lines of force. If the components of the rotation are $\phi_x$, $\phi_y$ and $\phi_z$ then

$$\tan 2\phi_x = \frac{2a_{23}}{a_{22} - a_{23}}, \qquad \text{etc.,}$$

or

$$\tan 2\phi_x = \frac{2e_{41}P_x}{b_0^2 - c_0^2} = \frac{K_x - 1}{2\pi(b_0^2 - c_0^2)} \cdot e_{41}X. \tag{16}$$

Values given by Pockels to the constants of Rochelle salt are:

$$e_{52} = -10.8 \times 10^{-8}; \qquad e_{63} = +2.1 \times 10^{-8}.$$

He remarks that the value of $e_{41}$ could not be definitely determined because of the strong internal conductivity in this direction, but still that it was found to be negative and of the same order of magnitude as $e_{52}$ or perhaps greater. In some cases of other crystals he was able to calculate how much of the effect was due to electric deformation, but in the case of Rochelle salt the necessary data on elastic constants and piezo-optic coefficients was lacking. The sign of $e_{63}$, however, is opposite to what it would be if all the effect were due to electric deformation so that there is surely a direct electro-optic effect in this case at least.

In the ă direction Pockels found also an increase in double refraction, *i.e.*, a Kerr effect, and states that this might be related to the large internal conductivity in this direction. The conductivity of the crystal is, however, not particularly large under ordinary conditions as the preceding pages show.

The present work is concerned with the variation in the electro-optic effect near the upper, more accessible, critical piezo-electric temperature range. Whereas Pockels calculated the rotation of the principal axes by observing the change in double refraction in some known direction in the plane normal to the field, the writer sought to measure the effect more directly. The most convenient arrangement was considered to be one in which transparent electrodes were applied to the faces of the crystal so that observations could be made in the direction of the lines of force. For this purpose, alcohol electrodes were used since this substance does not dissolve the crystal while its conductivity is $10^5$ times as great as that of Rochelle salt at the temperatures employed. The arrangement used in mounting the crystal plate is shown in Fig. 5. A difference of potential was applied between the platinum rings *BB* which were near the crystal and in the tubes containing the alcohol. The crystal was clamped between the rubber tubes *CC* by the screws *DD* running through the hard rubber blocks *EE*. The plane-parallel windows *AA* were cemented on with paraffin. A thermocouple T.C. came under one of the rubber tubes close to the crystal. To minimize electrical leakage over the surfaces the plate was made as large as possible so as to present a maximum distance around the edges. The alcohol had to be free of water so as not to spoil the faces of the plate. The difference of potential was applied and measured by the same scheme as used in the conductivity measurements.

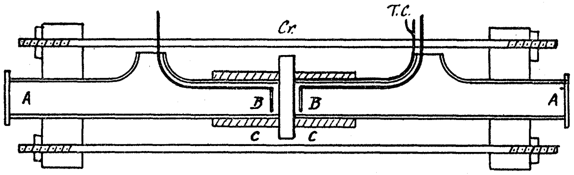


Fig. 5.

The monochromatic light used in the measurements was furnished by a Hilger wave-length spectrometer in connection with an arc light. For most purposes the brightest illumination obtainable gave the best results. This proved to be the yellow-green of 5737 Å. A lens and nicol prism were placed in the beam so that plane polarized parallel light could be transmitted through the crystal plate in the direction of the applied field. The resulting elliptically polarized light was analyzed by A. Q. Tool's modification[1] of Stokes's analyzer which was kindly loaned to the writer by the University of Nebraska.

For any crystal plate with relative retardation $\delta$ and orientation $\phi$ with respect to the plane of polarization of the incident light, the angle $\omega$ whose tangent is the ellipticity is given by the equation:

$$\sin 2\omega = \sin 2\phi \sin \delta. \tag{17}$$

For a Stokes's analyzer of compensator order $\pi N_1$ which is set on this ellipse we have:[2]

$$\sin 2\omega = \sin 2\pi N_1 \cos n,$$

where

$$\cos 2\pi N_1 = \frac{\tan n}{\tan c} \tag{18}$$

and $n$ and $c$ are respectively the differences between complementary compensator and nicol settings. Combining these two equations and differentiating, we find that:

$$-\sin 2\pi N_1 \cdot \sin n \cdot \Delta n = 2 \cos 2\phi \cdot \sin \delta \cdot \Delta\phi + \sin 2\phi \cdot \cos \delta \cdot \Delta\delta. \tag{19}$$

Suppose that the plate is set so that $\phi = 0$. Then if the compensator is very nearly a quarter wave plate and the ellipticity is small so that $n$ is nearly $\pi/2$, we have as more or less of an approximation according to the accuracy with which these conditions are fulfilled:

$$\Delta n = 2 \sin \delta \cdot \Delta\phi. \tag{20}$$

The relative retardation $\delta$ can be calculated from the indices and the thickness of the plate. For the best accuracy the thickness should be such that sin $\delta$ is nearly unity. The value of $\delta$ is given by:

$$\delta = \frac{2\pi d}{\lambda}(n_1 - n_2). \tag{21}$$

For light of wave-length 0.00005737 cm., $\delta$ is equal to 19.75 $d$, so that $d$ should best be 2.00, 2.15, 2.31, 2.47, etc., millimeters and not 2.39, 2.55, etc. At the proper thickness a change in $\delta$ has a negligible effect on $\Delta n$ as equation (19) shows. By choosing such a thickness, errors due to temperature and ordinary electro-striction are eliminated.

A suggestion for improvement in apparatus and method is to mount the crystal on a graduated circle, and, having set the analyzer for plane polarized light, find the rotation of the crystal necessary to restore it. This would measure the angle $\Delta\phi$ directly. The writer did not have a circle available to carry this out.

---

[1] Tool, Phys. Rev., XXXI., p. 1, 1910.

[2] Tuckerman, Univ. of Nebr. Studies, IX., No. 2, 1909.

The results of the observations are presented in Fig. 6, curve *A*. The ordinates give the rotation in degrees of the $\alpha$ and $\beta$ axes in their plane per volt per centimeter normal to them. The fields used were about 8,000 volts per centimeter. The rotation reverses with the direction of the field and bears a right-hand screw relation to the directions of the lines of force. Referring to equation (16) the constant $e_{41}$ was found to have the values:

$$- 1.94 \times 10^{-8} \text{ at } 20^\circ \text{ C.},$$
$$- 2.66 \times 10^{-8} \text{ at } 25^\circ \text{ C.},$$
$$- 2.76 \times 10^{-8} \text{ at } 30^\circ \text{ C.}$$

In computing these, the fields were put in electro-static units and the values of the dielectric constant used were those determined by the writer and are plotted in Fig. 6, curve *C*.

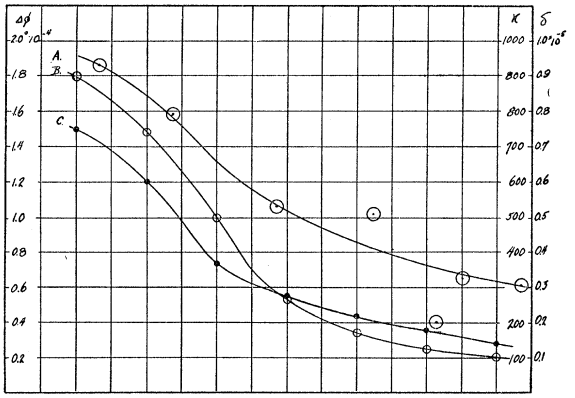


Fig. 6.

There is a decided decrease in the angular rotation as the temperature changes from 20 to 30° C. and the field is kept constant. To show the variation in piezo-electric modulus and dielectric constant in the same range, curves *B* and *C* are drawn. A comparison with curve *A* shows that the decrease in electric-optic rotation is less than that of either the piezo-electric modulus or the dielectric constant, although it is more nearly equivalent to the latter. Indeed, one observes that $e_{41}$, which refers to the rotation per unit polarization, increases continuously throughout this range.

This is a very striking result in view of the fact that the piezo-electric modulus decreases so appreciably. If the elastic coefficients and the piezo-optic constants do not change then the portion of the electro-optic effect due to electric deformation decreases in the same manner as the piezo-electric moduli. The direct effect of the field on the vibrations of the dispersion charges would then necessarily increase and soon give nearly the whole effect. As this is improbable, it seems that there is a decided change in the elasticity or the piezo-optic coefficients or both. In the absence of definite data on these quantities no more can be said at present. The writer inclines to the view that an increase in elastic constants occurs sufficient to account for both the variation in the piezo-electric moduli and the increase in the electro-optic effect.

## Pyro-electric Effect.

Although Rochelle salt is classed as a type of crystal that should give no pyro-electric effect, still the existence of a measurable polarization in the $\breve{a}$ direction makes it possible that such an effect can be observed. The greatest difficulty in measuring it is the danger of exciting a piezo-electric effect due to non-uniform heating. Customarily, the charges which appear on the faces of the crystal are measured between two steady temperatures so that these errors tend to cancel out. Due to the difficulty of producing liquid insulating baths of steady temperature in the range to be investigated and because of the likelihood of leakage, a slow rate of heating was employed. The utmost precautions were taken to keep the heating uniform. The crystal plate was made circular so that the residual thermo-elastic stresses would have a symmetrical distribution and balance their piezo-electric action. This plate was suspended by the leads inside two concentric cylinders of brass. Copper diaphragms and plugs of wool in the ends served to make the temperature distribution uniform. To test the symmetry of the heating, measurements were made with the crystal in two positions at 90° to each other so as to give the complementary distribution of stresses. This just reversed the error due to the piezo-electric effect.

The charge was measured as it appeared on the faces, beginning at − 70° C., by an electrometer compensating system. This always kept the faces of the crystal nearly at zero potential and eliminated leakage to a large extent. In Fig. 7 several curves are shown which give as ordinates, the pyro-electric charge developed between − 70° C. and the temperature plotted as abscissa. Curve *C* gives the results obtained with the crystal rotated 90° to its previous position.

Attention is rather called to the general nature of these curves than to numerical values although it may be noted that the electrode area was 1.44 cm.$^2$ The piezo-electric error has been largely eliminated for it will be observed that the results were very similar in the complementary positions mentioned above. In addition to this, the variation with temperature does not approach the magnitude of that shown by the piezo-electric charge for constant stress. The heating rate was constant and this should have made the stresses nearly constant. These facts all point to the pyro-electric character of the charge measured.

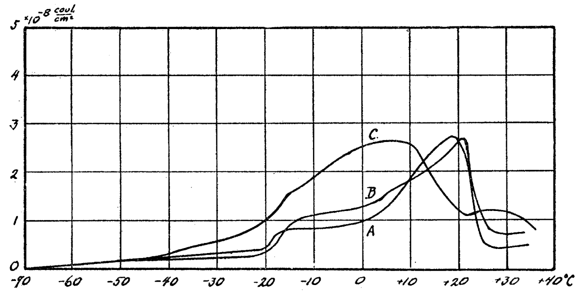


Fig. 7.

Since the dilatation of the crystal varies uniformly, this charge cannot be accounted for by expansion and it is therefore what is termed a "real" pyro-electric effect. The pyro-electric coefficient or change in surface density of charge, which is proportional to the derivative of the curves shown, evidently reverses sign just below room temperature and becomes very large. The existence of a real pyro-electric effect is of special interest because of its apparent non-existence from data obtained on other crystals.[1] It may be advisable to make a quantitative determination by some accurate method.

## Neumann's Principle.

In the case of Rochelle salt the mere existence of any kind of polar effect is of great interest because of the symmetry of the crystal form. Rochelle salt is always classified as a hemihedral orthorhombic crystal. It does not have any polar symmetry in its crystal form and hence should have no directed physical properties. This conclusion is based on Neumann's principle[2] which is a very fundamental hypothesis in crystal physics. It states that the physical properties have always at least the symmetry of the crystal form. Applications of this principle are extensively used to reduce general physical formulæ to their simplest form for any particular type of crystal form.

If Rochelle salt is really in the hemihedral class of the orthorhombic system, then much of the data collected by the writer and others disprove the exactness of Neumann's principle. There are various effects so far studied that show a definite polarity in the ă crystallographic direction. In the first place there are the condenser charge and discharge throws

---

[1] Lindemann, Ann. d. Phys., 62, No. 2, 107, 1920.

[2] Voigt, Krystallphysik, p. 3 and p. 20.

which Anderson[1] first showed were different in the two directions, together with the unsymmetrical hysteresis loops that grew out of the writer's[2] study of Anderson's experiments. Secondly, the piezo-electric property in various electric fields shows a decided dependence on the direction of the field. Then there is also the unidirectional conductivity at some temperatures, and finally there is good evidence for the existence of a pyroelectric effect. This proves conclusively that Rochelle salt has directed electrical properties in the ǎ direction.

It may be that a careful study of the crystal form will show that it is not hemihedral but possibly hemimorphic and thus save Neumann's principle. All of the work done by the writer has been on material furnished by two large crystals presented by Dr. W. R. Whitney of the General Electric Company. A record of a rough crystallographic examination of the first one to be used up did not contain any reference to a polar structure. The second crystal, examined more recently, does show something that points in this direction and was not noticed at first. A drawing of the base of the crystal is shown in Fig. 1*B*. The faces indicated are all prism faces, no pyramids being present, the ends of the c axis being bounded by pinacoids. The sphenoidal faces were not present. It will be observed that the ǎ direction has on one side a very narrow face normal to the axis, while the other side is bounded by sloping planes. In other respects the planes occur in closed groups unless one considers the few irregularities in flatness on some of the broader faces.

If Rochelle salt is hemimorphic much of the work done on its properties will be incomplete, since all of the coefficients pertaining to any physical property would not be known. To find these would necessitate measurements in several other known directions suitably chosen with respect to the crystallographic axes. The complete set of coefficients would then appear as solutions of a set of simultaneous linear equations. The number and character of the coefficients to be determined will depend on the symmetry of the physical agency and the reaction to which it is related. These are classed by Voigt[3] as scalars, *e.g.*, temperature; vectors, *e.g.*, fields; and tensor tripels, *e.g.*, stresses or strains. Thus piezo-electric phenomena consist of relations between a tensor tripel, stress, and a vector, electric polarization. This type of relation requires in general eighteen coefficients for its complete specification. The three components of polarization are expressed by Voigt as linear functions of the six stress components as follows:

$$P_x = \delta_{11}X_x + \delta_{12}Y_y + \delta_{13}Z_z + \delta_{14}Y_z + \delta_{15}Z_x + \delta_{16}X_y, \quad \text{etc.}$$

---

[1] Anderson, Report to the National Research Council, Mar. and Apr., 1918.

[2] Valasek, Phys. Rev., XVII., p. 475, and XIX., p. 478.

[3] Voigt, Krystallphysik, p. 122.

In the orthorhombic system the piezo-electric moduli are reduced by Neumann's principle to the following sets:

I. Hemimorphic Group ($A_z^2$, $E_x$)

$$\begin{array}{cccccc} 0 & 0 & 0 & 0 & \delta_{15} & 0 \\ 0 & 0 & 0 & \delta_{24} & 0 & 0 \\ \delta_{31} & \delta_{32} & \delta_{33} & 0 & 0 & \delta_{36} \end{array}$$

II. Hemihedral Group ($A_z^2$, $A_x^2$)

$$\begin{array}{cccccc} 0 & 0 & 0 & \delta_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \delta_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & \delta_{36} \end{array}$$

This brings up a consideration that places another aspect on the situation. A plate normal to the ă axis will give, in the first system above, a charge *only* when subjected to a $Z_x$ shear. Measurements made on a plate so oriented show under a $Y_z$ shear, the large piezo-electric effect characteristic of Rochelle salt. This seems to prove that Rochelle salt belongs to the hemihedral group since these results are in keeping with the nature of the second system of moduli given above and not in agreement with the first.

This contradictory array of facts is very puzzling, for their validity cannot be doubted. Perhaps, after all, Neumann's principle is only approximately true or probably not as general as it has been supposed to be. One may say that the crystal is made more or less polar by the physical agency applied, but this is only another way of saying that Neumann's principle is not exact or that it holds only in the limit when the stresses or fields are very small.

## PIEZO-ELECTRIC THEORY.

There have been several explanations proposed for the piezo- and pyroelectric phenomena. In order to account for pyroelectricity, Lord Kelvin[1] assumed the elements of the crystal structure to be permanently polarized. Under ordinary conditions surface charges compensate for their induction at external points, but when the temperature changes the moment alters, and free charges appear on certain faces. Riecke[2] generalized this idea to account for piezo-electric phenomena as well. His "crystal molecules" consisted of rigid pole systems of specified form instead of a simple dipole. A compression or temperature change would alter the distance between them and thus change the moment and cause the appearance of charges.

---

[1] W. Thomson, Phil. Mag. (5), 5, p. 26, 1878.

[2] Riecke, Nach. Ges. d. Wiss. Gott., 1891.

Later Voigt[1] modified Riecke's theory by assuming that the pole systems could be distorted. One advantage of this view is that a permanent polarization is made unnecessary. This is in better harmony with experiment. Phenomena which would accompany a high surface density of charge demanded by Riecke's theory have never been observed. Moreover, Voigt showed that the permanent polarization in tourmaline is small and equal to the pyro-electric response for a change in temperature of only 26° C. Thus he found that the permanent polarization became zero if the crystal was heated to 50° C. The writer[2] has measured the permanent polarization of Rochelle salt in the $\breve{a}$ direction and also found that it is of the order of magnitude of variations in it. It is equal to the piezo-electric excitation for one hundred grams or equal to the polarization produced by a field of only 15 volts per centimeter. Applied fields of between $-1600$ and $+1600$ volts per centimeter decidedly change and even reverse the direction of this polarization while they do not reverse the piezo-electric response at all. They merely change its value in such a way that it approaches zero for large fields of either sign. This shows that the changes in polarization represented by the piezo- and pyroelectric effects are not dependent on the existence of a permanent polarization.

An explanation based on different assumptions was first made by the Curie brothers[3] and developed later by Lord Kelvin.[4] The basic idea is that the crystal molecules consist of connected dissimilar parts having definite contact differences of potential. Any orderly arrangement of such rigid crystal elements connected by quasi-elastic forces acting like elastic non-conducting springs, will take on a definite charge distribution due to the contact differences of potential and depending in amount on the capacities between the various parts.

A distortion of such an arrangement will change the capacities and cause changes in the potentials of insulated plates on the faces of the crystal. Lord Kelvin points out in detail how such a mechanical model can be made to give any desired value to the twenty-one piezo- and pyroelectric coefficients and satisfy any type of crystal. A real pyroelectric effect may also be produced in this model by the distortion of certain springs by the temperature, so that even if the faces are fixed, the inner molecules rotate.

On either Riecke's or Lord Kelvin's theory, a varying piezo-electric effect such as occurs in Rochelle salt at certain temperatures would

---

[1] Voigt, Nach. Ges. d. Wiss. Gott., 1893.

[2] Valasek, Phys. Rev., XVII., p. 480.

[3] J. and P. Curie, C. R., *92*, 352, 1881.

[4] W. Thomson, Phil. Mag. (5), *36*, 453, 1893.

arise from a change in either the crystal structure or the forces between crystal elements. Circumstances tending to alter the grouping of these elements are known to have pronounced effects on the piezo-electric property, but such alterations in the structure in the two critical temperature ranges of Rochelle salt do not occur. For example, between − 20 and − 30° C., the piezo-electric activity decreases a thousand fold with no noticeable variation in heat absorption, dilatation, or refraction. These surely would change if the crystal form were altered.

The alternative is to suppose that the forces between crystal elements change at these temperatures. These forces are related to the cohesive forces and the elastic constants. They may vary either by changing the distances between the crystal elements or by changing their structure and hence their external field. A change in molecular structure likewise appears a little doubtful because of the constancy of the specific rotatory power. Probably this and other optical properties give no information on the piezo-electric structure because it does not involve charges with frequencies near the visible region. It appears that transformations in large ions or groups, and changes in the elastic properties of Rochelle salt occur to account for the variations in the piezo-electric activity, since these could not have been detected by the methods employed. The elastic constants await study.

If the x-ray analysis were not so difficult for this type of crystalline organic compound, it would be worth while to study the crystal structure and reflection coefficients by this means. The writer thinks that some of his previous work shows that the piezo-electric structure is intimately bound up with the water of crystallization. The place this occupies in the crystal structure and in crystal formation in general is therefore of great interest.

The writer expresses his gratitude to the National Research Council for the grant of a fellowship which enabled him to pursue this work.

Physical Laboratory,
University of Minnesota,
July, 1922.