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Master of Science . We recommend that the

degree of Master of Science be conferred

upon the candidate.

Minneapolis, Minnesota

_June 1,_____192 0   *W. F. Y. Swann*
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                               W. H. Bussey.
                               John F. Tate .
                               Henry A. Erikson

PIEZO-ELECTRIC AND ALLIED PHENOMENA

IN ROCHELLE SALT

A Thesis submitted to the Faculty of the Graduate School

of the

University of Minnesota

by

Joseph Valasek

in

partial fuXlfillment of the requirements for the degree of

Master of Science in Physics.

June 1920.

CONTENTS.

I. INTRODUCTION

(a) The Fundamental Phenomena.

In 1880, the brothers J. & P. Curie[*] observed that a plate
cut from crystalline quartz produced accumulations of electric
charges on opposite faces when subjected to a mechanical force.
This electro-elastic property they termed piezo-electricity. It
was soon found that many other crystals likewise exhibited this
interesting phenomenon, and it was shown that there also existed
a converse effect, in virtue of which, a piezo-electric substance
suffered a deformation when placed in an electric field. This
correlation between force and electric field, at least as far as
deformation is concerned, is worthy of note.

Of the thirty-two classes into which crystalline matter is
divided, according to the nature of their symmetry, there exists
in twenty, at least one axis, which is characterized by different
sets of faces on its opposite ends. Crystals which possess this
type of asymmetry all exhibit piezo-electric activity to a certain
degree. In these crystals, there are one or more axes at the ends
of which free charges are produced when the crystal is deformed
by mechanical force in some definite way. These axes are called
the piezo-electric axes.

As a result of investigations on a flat quartz plate, cut
from the crystal in such a way that its faces are normal to a
piezo-electric axis, P. Curie formulated the following statements:

(1) Equal and opposite charges are developed on the opposite
ends of a piezo-electric axis.

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(2)   The effect produced by a compression is equal and opposite to that produced by an equal tension.

(3)   Force applied perpendicular to the collecting plates produces a quantity of electricity which is directly proportional to the total force and is independent of the area of the face over which it is applied. This relation is expressed by the formula $q = \Delta'F$, where q is the quantity in electrostatic units, F is the force in dynes and Δ is a constant found by P.Curie to be equal to 6.32×10^{-8} e.s.u. per dyne for a quartz plate oriented as described.

(4)   For a force applied parallel to the collecting plates, i.e. on the ends of the crystal section, the charge is expressed by the formula $q = \Delta''F\cdot\frac{l}{d}$ where l is the length of the crystal in the direction of the force and d is the thickness, (i.e. the distance between the electrodes) and Δ is the same constant as above.

A simple qualitative explanation of the piezo-electric effect is given by Lord Kelvin.   He assumes the molecules of all piezo-electric crystals to be permanent electric doublets, and that the effect of a force is to change the molecular moment per unit volume by altering the distances between the molecules. This, he shows, produces free surface charges on the faces of the crystal. This theory is generally accepted and although it leads to no quantitative results, it gives a clear picture of the piezo-electric mechanism.

W. Voigt[*] , however, gives a theory which goes much farther then Thomson's.   By means of thermodynamic reasoning he shows

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[*] Voigt. Lehrbuch der Krystall Physik. p 80.

that the piezoelectric response on faces normal to the crystallo-
graphic axes 1, 2, and 3 (x,y,z) bears a linear relation to the
six elementary stresses, namely the three components of dilatation
X_x, Y_y, Z_z and the three components of shear Y_z, Z_x, X_y. This
relation is expressed by the formulae:

$$-\rho_1 = \delta_{11} X_x + \delta_{12} Y_y + \delta_{13} Z_z + \delta_{14} Y_z + \delta_{15} Z_x + \delta_{16} X_y$$

$$-\rho_2 = \delta_{21} X_x + \delta_{22} Y_y + \delta_{23} Z_z + \delta_{24} Y_z + \delta_{25} Z_x + \delta_{26} X_y$$

$$-\rho_3 = \delta_{31} X_x + \delta_{32} Y_y + \delta_{33} Z_z + \delta_{31} Y_z + \delta_{35} Z_x + \delta_{36} X_y .$$

The eighteen constants δ_{ik} are termed the piezoelectric moduli.
In every case except in that of the triclinic hemihedric group,
which has the highest degree of asymmetry, the number of these
constants is materially reduced. For example quartz has only
five of these moduli differing from zero and these are connected
by simple algebraic relations, leaving only two independent.
Rochelle salt, in which we are especially interested has only
three constants, its piezoelectric action being described by
the relations:

$$-\rho_1 = \delta_{14} Y_z$$
$$-\rho_2 = \delta_{25} Z_x$$
$$-\rho_3 = \delta_{36} X_y$$

From these equations it appears immediately that Rochelle salt
is active only with respect to the three components of shear
Y_z, Z_x, X_y about the crystallographic axes 1, 2, 3 which are
usually denoted as the $\overset{\circ}{a}, \overline{b}$ and $\overset{\prime}{c}$ axes. The three constants
in these equations have been determined experimentally by Pockels
who gives the following values:

$$\delta_{14} \sim 1000 \times 10^{-8} \quad e.s.u. /dyne$$
$$\delta_{25} = -165 \times 10^{-8} \quad " \quad "$$
$$\delta_{36} = +35.4 \times 10^{-8} \quad " \quad "$$

F. Pockels. Gottingen Abhandlungen   p 183   (1893)

He accompanies the value of $\delta_{,\nu}$ however with the remark that it
is merely a lower limit of the values observed. This makes
Rochelle salt, properly oriented, the most piezoelectrically
active substance known, being more than 150 times as active as
quartz.

(b) Recent Work Bearing on this Problem.

This great sensitivity of Rochelle salt has led to many
attempts to utilize its action in a practical way. Its properties
would appear to be valuable whenever it is desired to detect or
translate a small mechanical effect into an electrical effect
which can then be recorded or amplified in the usual way, if
desired. Some very recent work is this direction is excellently
reviewed by H. O. Wood[*] in his report of March 1919. The conclusion
arrived at is that Rochelle salt is anomalous in its behavior
and that it does not follow the simple theory outlined above
except in a very general way. The observations leading up to
this research will accordingly be briefly reviewed.

It has been observed by Cady[*] and others that crystal plates
of Rochelle salt, oriented in such a way as to exhibit the maxi-
mum effect, do not give a linear relation between force and piezo-
electric response as measured by a ballistic galvanometer. The
response, instead, increases more rapidly with the load for small
forces, while as the load is increased, the effect increases at a
less rapid rate. Curves, obtained by the writer, showing this
effect are given in Fig. 1. In the curves obtained by Cady the

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[*] H.O.Wood - Captain U.S.Engineers - Report - March 1919.
[*] Cady.   Report to National Research Council. May 1918.

FIGURE 1. a1a.

PIEZO-ELECTRIC RESPONSE
vs
FORCE

$T = 0°C$

$T = 23.2°C$

FORCE ~ GRAMS

$Q \sim 10^{-9}$ coulombs
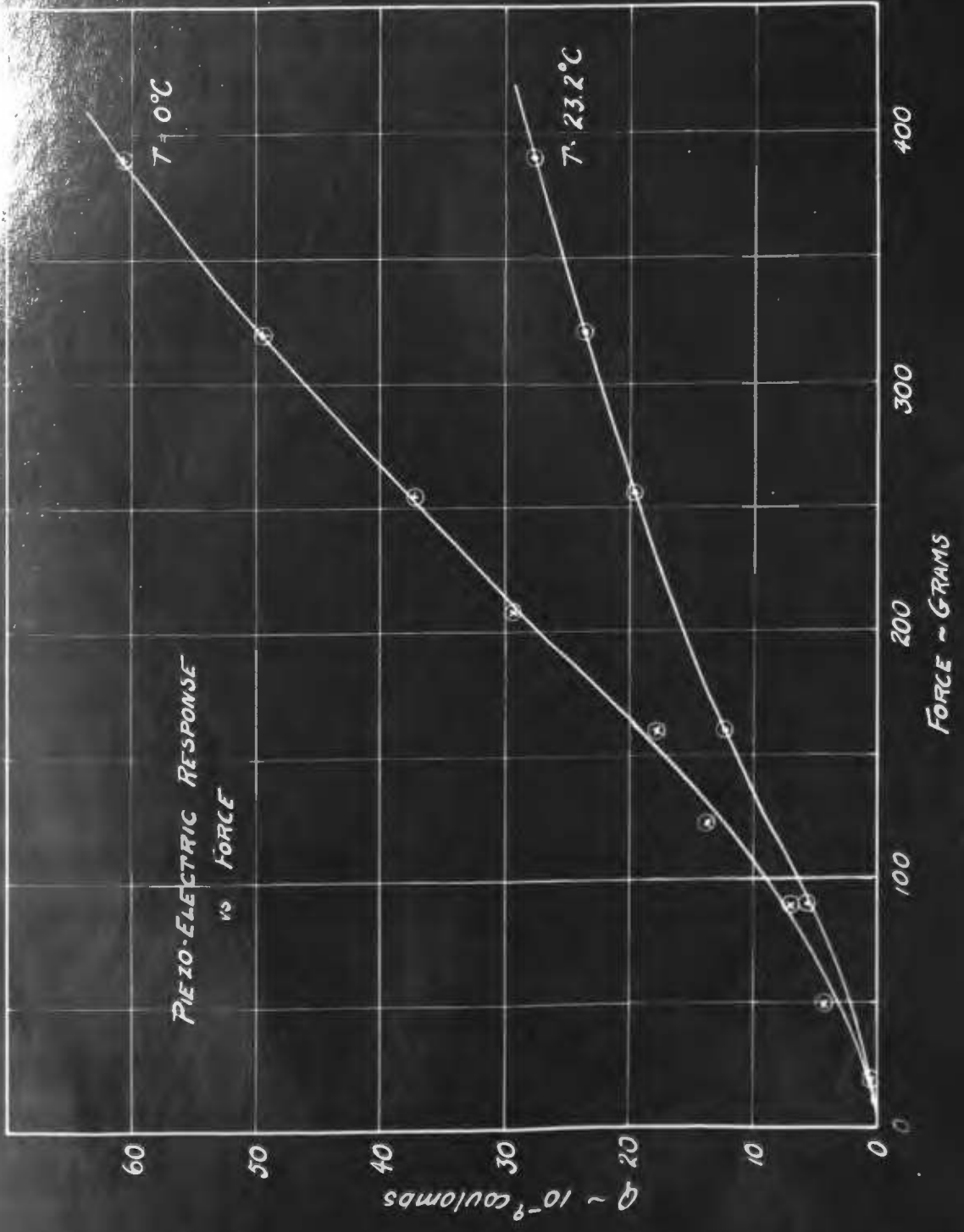
deviation from a linear relationship is much more marked. There
is moreover an effect of fatigue and even paralysis at high loads.
The response to pressure has been observed to deminish 60 o/o in
four minutes, due to fatigue. Temperature is another important
factor. The sensitiveness of a crystal diminishes 50 o/o for a
rise in temperature from 20° C to 25° C and decreases 60 o/o more
for a further rise of 5° C. It has also been observed that
humidity affects the results in a remarkable way. Although the
crystal is more sensitive in a moist atmosphere, the experimental
results are apt to be inconsistent unless the crystal surfaces are
thoroughly dry.

Experiments where made by J.A.Anderson[*] on the behavior of
Rochelle salt crystal plates used both as condensers and as piezo-
electric generators. He observed that the ballistic galvanometer
charge and discharge throws of the crystal used as a condenser
were unequal for fields of one sign, but that they were equal
and smaller for fields of opposite sign. He explains his obser-
vations on the assumption of a superposed electrostriction effect.
He also gives a set of curves showing the result of applying a
steady pressure to the crystal condenser and then observing the
charging throws. These curves have a maximum for fields applied
in one direction and fall off gradually for fields applied in the
opposite way. These results seemed, at that time, to be unexplain-
able.

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[*] Anderson. Reports to National Research Council March 1918 and
                                                    April 1918.

II.   AN EXPLANATION OF THE ANOMALIES RECENTLY OBSERVED.

The object of this research was to study the erratic be-
havior described above and to formulate, if possible, the necessary
extensions of the simple theory to cover these deviations.   It
was suggested by Dr. W. F. G. Swann that the first set of Anderson's
curves just discussed might be due to a hysteresis in the crystal.
This question was accordingly the first to be taken up and in-
vestigated.

On the doublet theory of dielectric action an electric field
produces a state of polarization in the medium.   One may picture
this to himself as a slight displacement of the electronic orbits
of each molecule with respect to the central positively charged
nucleus.   The amount of the resulting electric moment per cubic
centimeter is defined as the polarization of the dielectric and
is usually denoted by P.   The surface density of electric charge
produced by this polarization is likewise equal to P.   If E rep-
resents the electric intensity and D the dielectric displacement,
then the relation between D, E and P is expressed by

$$D = E + 4\pi P$$

The charge q on the plates of a parallel plate condenser is then
in general

$$q = \frac{\varkappa S}{4\pi d} \cdot V = \frac{S}{4\pi}(E + 4\pi P)$$

where the area of the plate is denoted by S and the distance
between the electrodes by d.   Since the charge and discharge
throws of the ballistic galvanometer are proportional to the
alteration in the quantity of electricity in the condenser, they
will give a measure of the change in the dielectric displacement D.

The case of magnetism is exactly analogous to that of a dielectric. If B represents the magnetic induction, H the field strength and I the intensity of magnetization, the relation between them is given by the formula B = H + 4πI. In this magnetic case it is a well known fact that B shows a "saturation" as H increases, and, moreover, that B goes through a hysteresis cycle for variations of H.

Because of the parallelism between dielectric action and magnetism, it appears at once that the unsymmetrical charge and discharge throws which were observed by Anderson can be explained by a hysteresis in P (and consequently in D). If this hysteresis loop is not symmetrical with respect to the origin, P will be nearer "saturation" for fields in the opposite direction to that applying above, and hence the throws would be smaller and more nearly equal. Curves, having these general characteristics have been obtained with iron as well as with Rochelle salt. The displacement with respect to the origin, postulated above, would mean that there is a ~~natural~~ polarization in the natural crystal. This polarization may be regarded as being identical with that which is required by Thomson's theory of piezo-electricity. A real test of this explanation would consist in attempting to obtain a hysteresis loop of D versus E for Rochelle salt. An interesting feature of this curve would be the displacement from the origin, giving the molecular electric moment of the crystal in its natural state.

The curves of D versus E as already noted, are not only unsymmetrical but they also approach saturation as E increases.

Thus if the curve $\frac{\partial^2 D}{\partial E^2}$ is plotted against E there will be a maximum for some value of E, corresponding to the point of most rapid increase of D with respect to E. This maximum will not be at zero, but at some E with a definite sign, because of the asymmetry of the first curve. It has already been remarked that the effects of force and applied electric field are equivalent in producing a piezoelectric deformation of the crystal. To the extent then that the force and field may be considered as equivalent in affecting the piezoelectric moment, we may expect that the relation between piezoelectric response for any given increment of force $\left(ie\ \frac{\Delta D}{\Delta F} \right)$ and the field E to be of the same nature as the relation of $\frac{\partial D}{\partial E}$ and E. Such was indeed found to be the case.
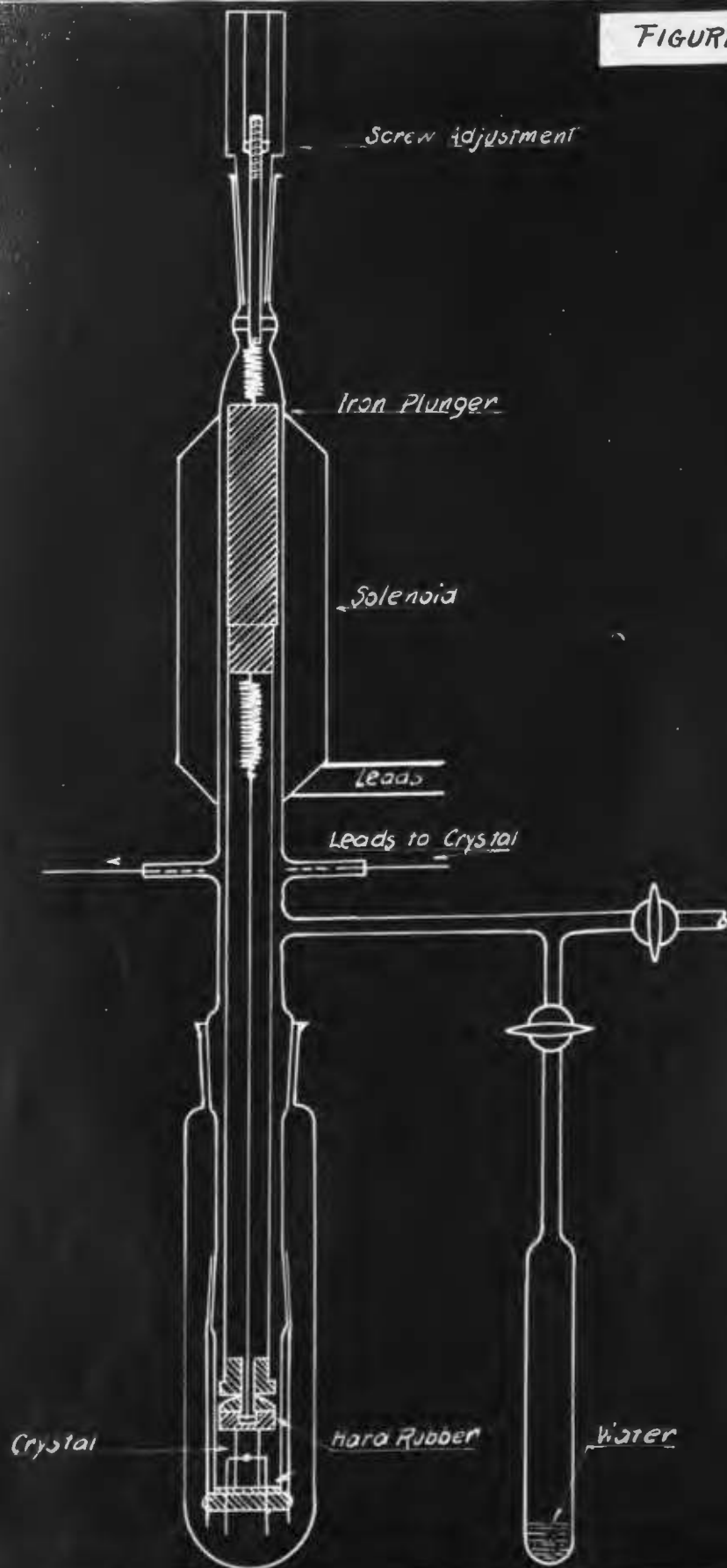
III.   EXPERIMENTAL VERIFICATION.

(a)   Apparatus and Technique.

In order to test these deductions an apparatus was constructed which would allow a simultaneous regulation of the various factors entering into the problem, as previously discussed. These factors are temperature, applied force, electric field, and humidity/ The variations in the electric charge on the electrodes of the crystal were measured by a Leeds and Northrup high sensitivity ballistic galvanometer.

The crystal and all directly connected parts were inclosed in a glass container as shown in the accompanying sketch, Fig 2. This allowed the apparatus to be evacuated or to be sealed off air tight, whenever desired, in order to preserve a constant

FIGURE 2. p.8a.

Screw Adjustment

Iron Plunger

Solenoid

Leads

Leads to Crystal

Crystal   Hard Rubber   Water

atmospheric condition.

The force mechanism consisted of a solenoid with an iron plunger at the end of a glass tube, which transmitted the compression to the crystal which was mounted on a hard rubber block directly below. The weight of the plunger and the effect of residual magnetism was compensated by a spring and screw mechanism which could be adjusted by means of a ground glass tap. These adjustments could be made at any time when the apparatus was sealed. The end of the glass rod was provided with a universal joint attachment made of hard rubber, which served to distribute the force uniformly over the ends of the crystal.

For regulating the humidity a bulb containing some water was attached to the body of the glass container. This bulb was immersed in a dewar flask which was usually filled with ice, thus giving a constant absolute humidity in the apparatus. The lower portion of the chamber containing the crystal was immersed well into a large dewar jar which provided heat insulation and also served as a means for the regulation of temperature by means of water baths and freezing mixtures. The temperatures were measured by two copper constantan thermocouples whose junctions were soldered to the tinfoil electrodes on the faces of the crystal. Two of the thermocouple wires also served as connections to the ballistic galvanometer and to the high voltage potentiometer arrangement which regulated the applied electric field. This consisted of a resistance of ten megohms, subdivided into ten equal parts. The various subdivisions were connected to a commutating switch and to the crystal and galvanometer as shown in Fig. 3. The working electromotive force was usually 800 volts so that the potential

FIGURE 3. p.94.

CRYSTAL

10 MEG OHMS
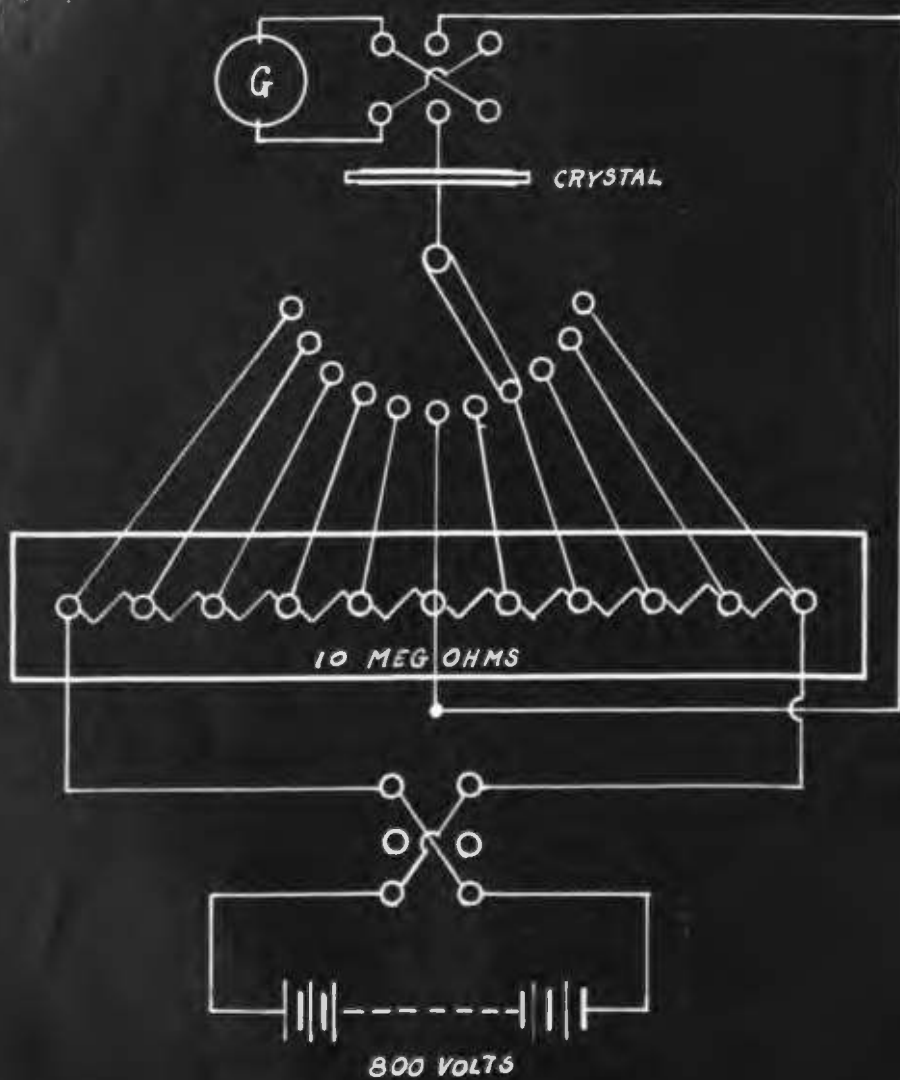
800 VOLTS

applied on the crystal could be varied from +400 to -400 volts
in steps of 80 volts each. The potentials used were measured
by an electrostatic voltmeter after each set of observations.

The crystal plates used were cut from a 100 gram crystal of
Rochelle salt which was grown and furnished by *Dr. Whitney of* the General Electric
Company. *to whom the author wishes to express his appreciation.* The plates were cut by a wet thread operating over two
pulleys and kept moist by running through a bucket of water *in the manner described by Cady* The
faces were dressed down and smoothened by a moist piece of ground
glass. The orientation of the faces was such as would give the
maximum response. The faces were, accordingly, perpendicular to *the x axis,*
the edges making angles of 45° with the $\overline{b}$ and c' axes. Figure
4 shows the various stages in the preparation of such a crystal
plate.   Compressing the ends of the section would accordingly
result in a shear in the $\overline{b}$ and c' directions (Y_z after Voigt).
Since the shears Z_x and X_y vanish for a uniformly stressed crystal
of this orientation, we are left with the effect due to Y_z alone,
namely $-P_1 = \delta_{14} Y_z$
The charge densities on the tinfoil plates cemented with shellac
to the crystal faces are accordingly equal to   and if we let
ℓ denote the length, b the width and d the thickness of the
section, the relation between the total charge q and the total
force on the end of the crystal (F) will be given by

$$-q = -b\ell p_1 = b\ell \cdot \delta_{14} \cdot \frac{F}{bd} \qquad or:- \qquad q = -\delta_{14} \cdot F \cdot \frac{\ell}{d}$$

which is identical with P. Curies formula with Δ replaced by its
equivalent $-\delta_{14}$. Since the relation between piezoelectric response
and pressure is not a linear one in the case of Rochelle salt, δ_{14}
will not be constant but will be in general some function of F.

FIGURE 4.
Preparation of Crystal Plates.

(b)   The Observations.

The behavior of the crystal as a condenser was first in-
vestigated and the conclusions as to a hysteresis in D were verified.
Measurements of D for cyclical changes in E gave typical hysteresis
loops.   They were, moreover, unsymmetrical as was to be expected
if the crystal had a natural polarization.   The exact character
of the loop was found to depend on moisture and temperature con-
ditions of the crystal.   Figure 5 shows the results of observations
at a temperature of 23° C and a relative humidity of 30 o/o.
Figure 6 gives a loop obtained at 0° C with the surfaces of the
crystal thoroughly dried.   The plate had been kept at this tem-
perature and under cover with phosphorus pentoxide for fifteen
hours before these observations were made.   After twenty four
hours more under these conditions there was practically no piezo-
electric activity and very little hysteresis, apparently caused
by excessive dryness.

It was also soon apparent that the response to pressure
showed a hysteresis with respect to changes in temperature, when
the absolute humidity was kept constant by the method described.
This appears to be due to a change in the moisture content of the
crystal which then alters its piezo-electric properties.   That
such variations in moisture occur was shown by keeping two crystal
plates in moist and dry atmospheres respectively and by occasionally
weighing them.   The changes in weight during the first four days
amounted to over 5 o/o.   These variations in moisture content at
any temperature are relatively slow so that it requires several
days for the approach of an equilibrium moisture condition, which

undoubtedly depends on the temperature. Such a variation appears to be the most probable cause of the temperature hysteresis loop which was observed.

Phosphorus pentoxide is too strong a drying agent to use in experiments with Rochelle salt, as it is sufficiently powerful to completely dehydrate the crystal after several weeks. This naturally causes it to lose its activity and it may even split open, as was observed in one case.

Curves showing the relation between electric field and piezo-electric response were obtained for a number of values of applied force. All of these curves show a maximum for an applied field of a certain sign, while they fall off gradually in the opposite direction in conformity with previous comclusions. These curves are reproduced in Fig. 7.

Anderson has obtained a set of curves somewhat similar in character by observations on the charge of the crystal condenser when under pressure. The results, the explanation of which he finds so difficult, may likewise be attributed to the equivalence of force and electric field in producing a change in the polar-ization of the crystal. Since the curve of D versus F approaches saturation in both directions, the derived curve $\frac{\partial D}{\partial F}$ will have a maximum somewhere, and since ΔD corresponding to a given change in electric field ΔE, will have the same characteristics as a ΔD produced by a ΔF, it will also have a maximum displaced with respect to the origin.

Anderson: Local citation.

FIGURE 5   p.11a

HYSTERESIS LOOP
ELECTRIC FIELD vs CHARGE

ELECTRIC FIELD   volts/cm.

CHARGE ~ 10⁻⁹ coulombs

FIGURE 6   p.116.

HYSTERESIS LOOP

ELECTRIC FIELD vs CHARGE

QUANTITY ~ 10^{-4} coulombs

ELECTRIC FIELD ~ volts per centimeter

FIGURE 7.   p. 12a.

PIEZO-ELECTRIC RESPONSE
vs
ELECTRIC FIELD

(1) FORCE   140 gr.
(2)   "   350 "
(3)   "   600 "
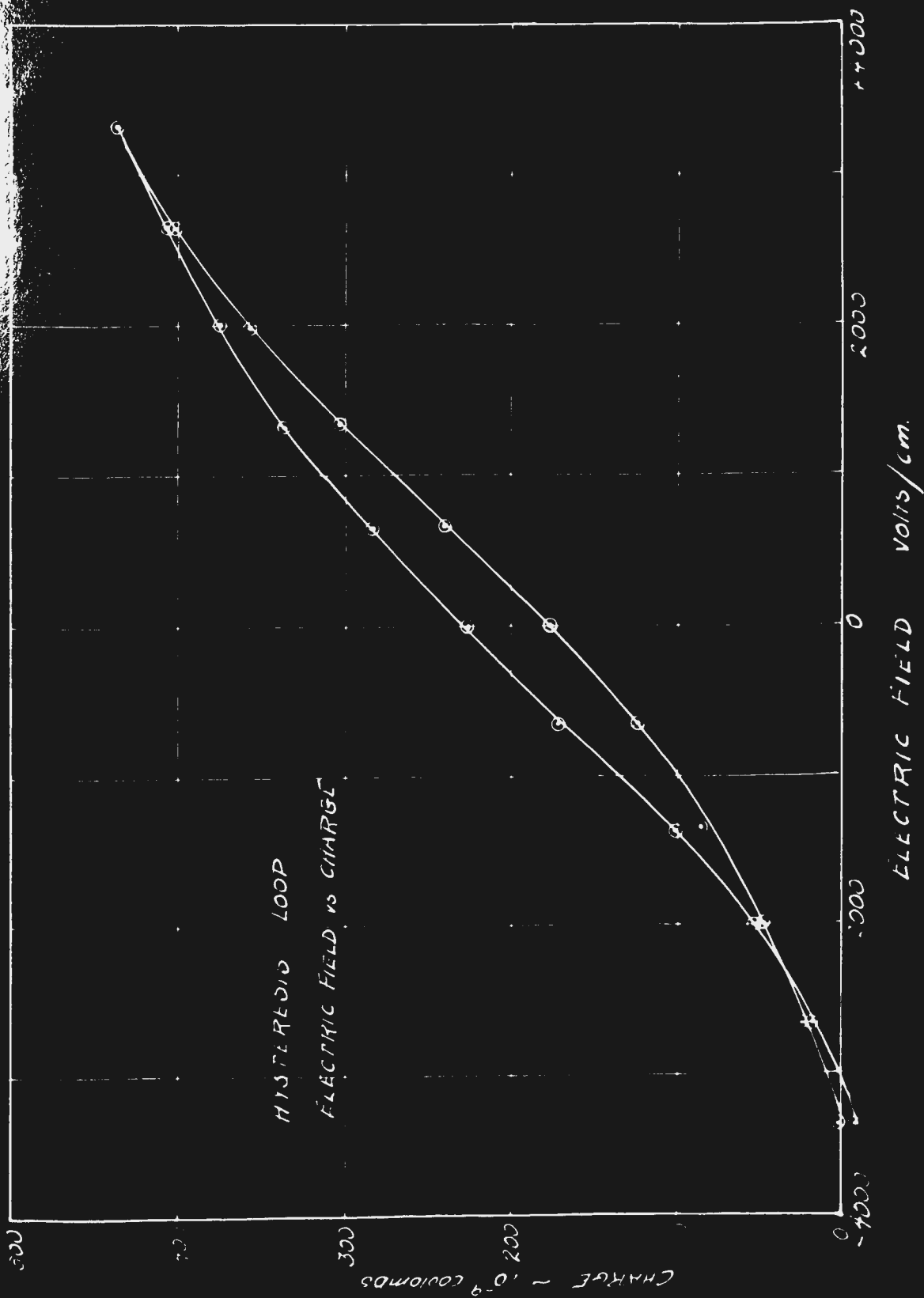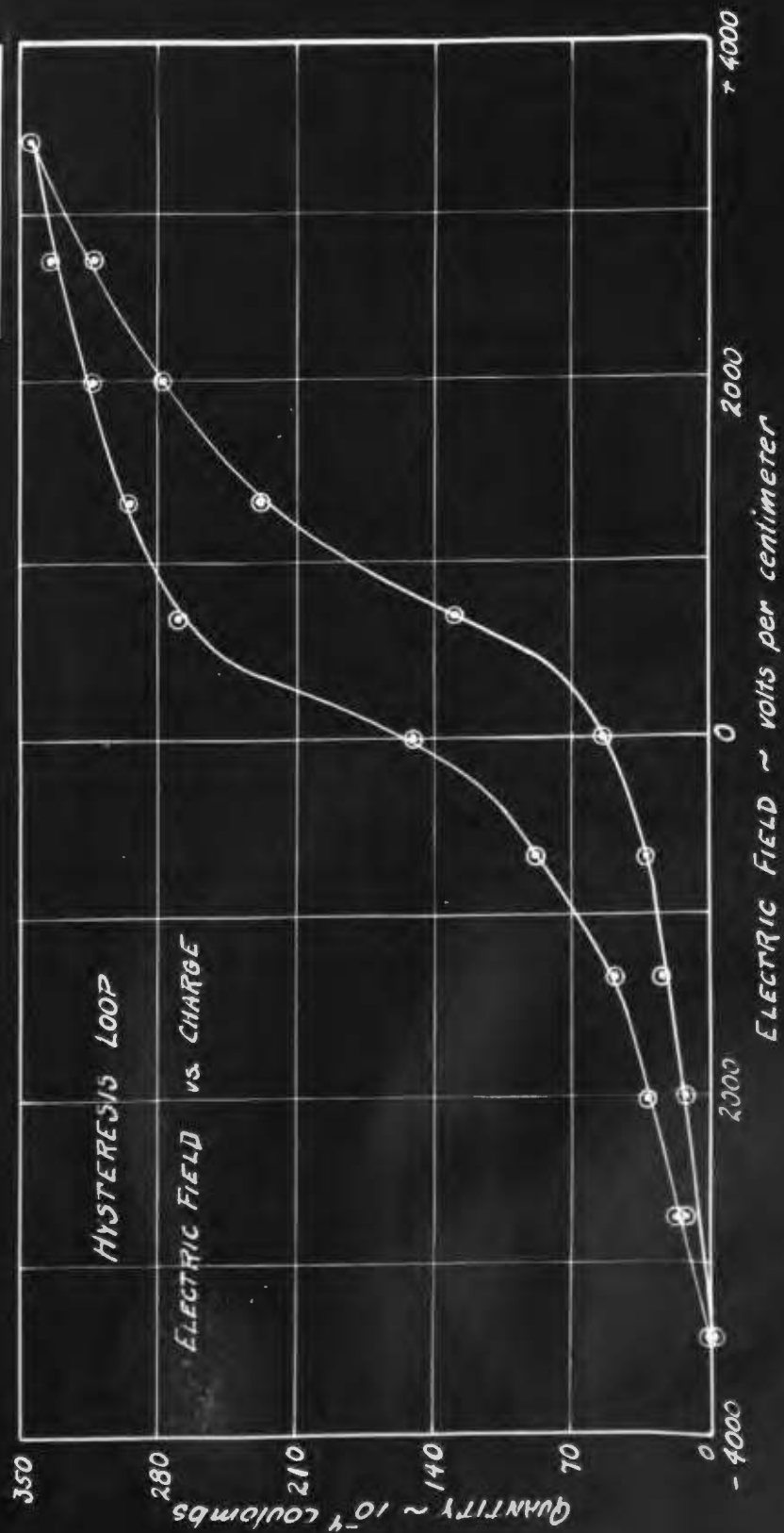(4)   "   880 "

QUANTITY ~ 10⁻⁹ coulombs

ELECTRIC FIELD ~ volts per centimeter
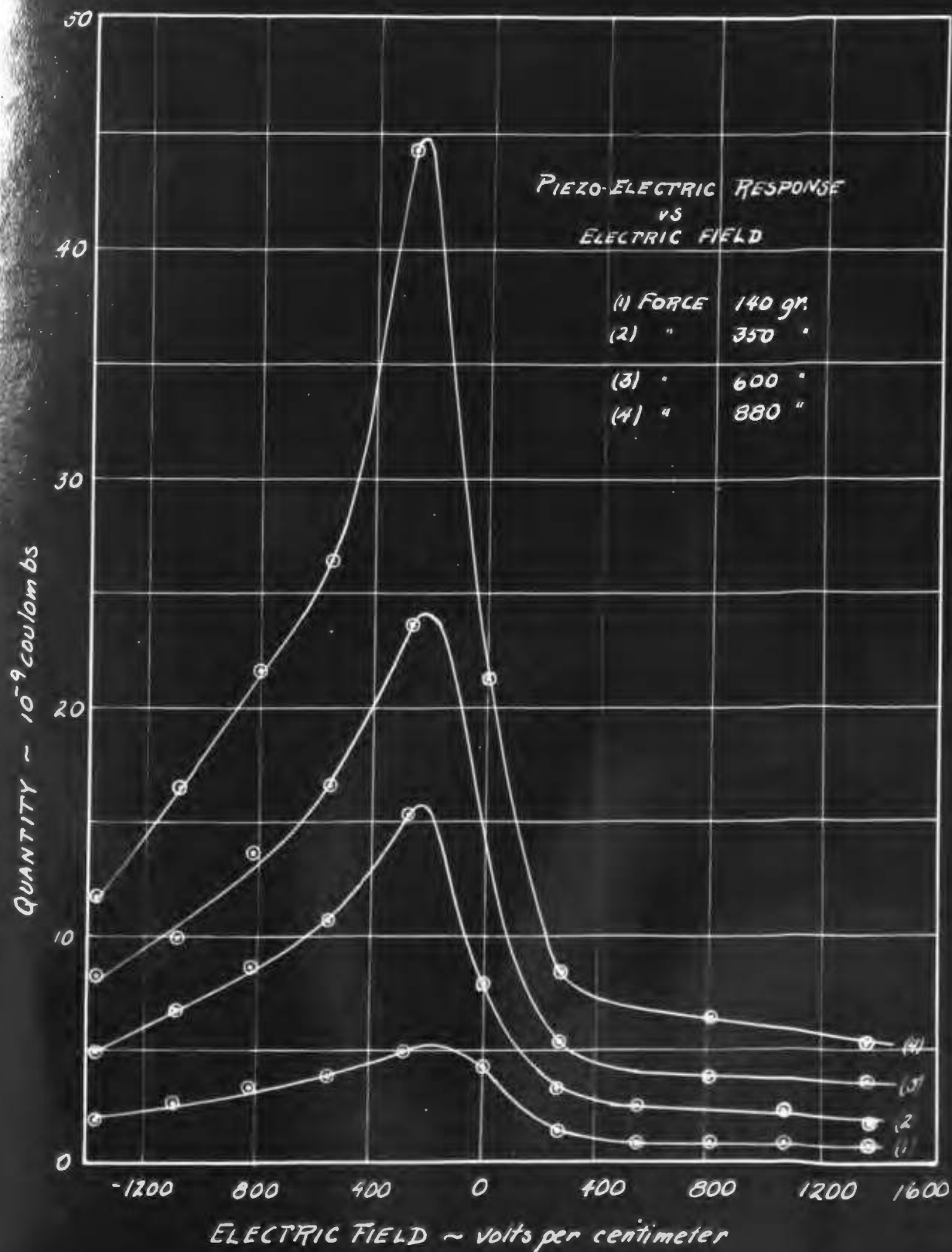
IV. CONCLUSION.

From the observations given, the dielectric, and some of the piezoelectric constants of Rochelle salt may be calculated. The values are markedly dependent on the temperature and humidity, on the time exposed to these conditions and also on the electrical and mechanical treatment of the crystal just preceding the observations. Accordingly, no accurate figures can be given, since the precise interrelations of these variables is as yet unknown. The order of magnitude of the effects may however be obtained.

From the asymmetry of the hysteresis loops, the natural molecular electric moment was found to be $16,$ $\frac{e.s.u.}{cm^2}$ at a temperature of 33° C and a relative humidity of 30 o/o. It was found to have increased to $85,$ $\frac{e.s.u.}{cm}$ at 0° C and in a very dry atmosphere (over P_2O_5 for 15 hours).

The dielectric constant showed extremely large variations under the different conditions. The lowest value observed was 46 and the highest was 550. Cady gives a value of 80 and remarks that the dielectric "constant" of Rochelle salt does not appear to be constant by any means. The greatest variation observed was with respect to the applied field under certain conditions

The piezoelectric constant calculated from that portion of the force versus response curve which is straight and which is also the steepest portion (Fig. 1) gives $8.85 \times 10^{-5} \frac{e.s.u.}{dyne}$ for the value of δ_{14} at a temperature of 33° C and a relative humidity of 30 o/o, and $18.0 \times 10^{-5} \frac{e.s.u.}{dyne}$ at 0° C and a dry condition (over P_2O_5 - 15 hours) Cady has previously assigned a range of $3.4 \text{ to } 40. \times 10^{-5} \frac{e.s.u.}{dyne}$ for this constant.

There is, of course, much work still to be done on this problem. A systematic study should first be made of the effects of humidity, temperature and pressure on the piezoelectric and dielectric properties of Rochelle salt. It would also be interesting to learn whether the changes in piezoelectric response under different conditions may be traced to changes in the elasticity of the crystal. Dr. Swann has also suggested that X-Ray spectrographs of the crystal in action would probably reveal some interesting information because of the very high dielectric constant, which would involve large atomic deformations. A study of the exact effect of surface moisture on the piezo-electric effect seems to offer some interesting possibilities. In some cases the response has been observed to diminish 50 o/o in three minutes after decreasing the humidity of the air in the apparatus. The moisture content inside the crystal can hardly change so rapidly. This suggests a surface moisture piezoelectric effect which would appear to play an important part in the activity of Rochelle salt.

V. SUMMARY.

The results of this research may be briefly summarized as follows:

(1) A parallelism is shown to exist between the action of Rochelle salt as a dielectric and of iron as a ferromagnetic substance. Hysteresis loops of dielectric displacement versus electric intensity are obtained.

(2) It is shown that piezoelectric response shows a hysteresis with temperature at a constant absolute humidity.

(3)   The effects of pressure and applied electric field
are shown to be equivalent, to a certain degree, in producing
a change in the piezo-electric moment.   Curves giving the
relation between piezo-electric response and applied field
are presented.

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