PIEZO-ELECTRIC AND ALLIED PHENOMENA IN ROCHELLE SALT.[1]

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Synopsis.

Electric Hysteresis in Rochelle Salt.—On the doublet theory of dielectric action, the dielectric displacement D, electric intensity E, and the polarization P are analogous to B, H, and I in the case of magnetism. Rochelle salt shows an electric hysteresis in P analogous to the magnetic hysteresis in the case of iron. The loops obtained are displaced from the origin by an amount which gives a measure of the *permanent polarization in the natural state.* The moment per unit volume in the natural state is of the order of 50 e.s.u./cm.^{2} under ordinary conditions, this being about 13.3×10^{-21} e.s.u./cm.^{2} per molecule.

Piezo-electric Response of Rochelle Salt in an Electric Field.—Mechanical force and electric field are to a certain extent equivalent in producing a change in the piezo-electric moment. Measurements of the piezo-electric response in various applied fields therefore give curves of the same nature as the curves of dD/dE against E. Accordingly they show maxima displaced from the origin by the effect of permanent polarization.

R ECENT work on the piezo-electric and allied properties of Rochelle salt has brought to light a number of peculiarities in the electrical reactions of this substance to applied forces and electric fields. A survey of these effects is given by Capt. H. O. Wood in a report dated March, 1919. In the first place, observations by Cady[2] show that the piezo-electric response, or quantity of electricity set free by a pressure is not proportional to the force, as is demanded by the commonly accepted theory of piezo-electricity. Initially the response is more nearly proportional to the square of the force, subsequently increasing less and less rapidly and finally tending toward more or less of a saturation value. Investigating the action of the crystal as the dielectric in a condenser Anderson[3] has found that instead of the usual relation $Q = CV$ between the charge and the applied electromotive force, there exists a more complicated relation much like that described above as holding between piezo-electric response and applied force. The capacity of the condenser and hence also the dielectric constant of Rochelle salt thus appears to be a

[2] W. G. Cady, Report to National Research Council, May, 1918.
[3] J. A. Anderson, Reports to National Research Council, March and April, 1918.

function of the applied electromotive force. Moreover Anderson found that the ballistic galvanometer charge and discharge throws were unequal for fields of one sign but smaller and equal for fields of the opposite sign. In explanation he suggests that an electro-striction effect enters into and modifies the action of the crystal as a condenser. It appears however, that these results can be accounted for by a hysteresis in the crystal similar to ferromagnetic hysteresis, in a manner suggested by Professor W. F. G. Swann, as follows:

On the doublet theory of dielectric action, the dielectric displacement D, electric intensity E, and the polarization P (moment per unit volume) are analogous to B, H, and I in the case of magnetism. They are connected by the relation $D = E + 4\pi P$, and the charge Q of a parallel plate condenser of plate-area S is equal to $Q = S(E + 4\pi P)/4\pi = (S/4\pi)D$. The alteration in the charge density on the plates of the condenser is thus a measure of the alteration in the dielectric displacement D. A hysteresis in P and consequently in D would show itself in measurements of the charge on the condenser. A permanent polarization, such as is demanded by Lord Kelvin's theory, would be made measurable by a displacement of the center of the loop with respect to the origin. When this original polarization is disturbed, a restoring force is brought into play and it appears from experiments on fatigue of Rochelle salt crystals that the restoration of the permanent polarization takes place quite gradually. Suppose then, that the original condition of the crystal is represented by some point on, or near, the upper right-hand part of the hysteresis loop. A field tending to decrease the natural polarization will bring into play a larger hysteresis effect, causing the charge and discharge throws to be unequal to an extent depending on the rapidity with which the restoring force acts. For throws in the opposite direction, however, there will be less of a hysteresis effect and the throws will be more nearly equal. When these conditions were imposed on iron in a magnetization experiment, curves like Anderson's were obtained.

In the apparatus set up to verify this hysteresis effect provisions were made for the regulation of temperature and humidity as well as applied force and electric field. Rochelle salt is often very sensitive to slight changes in the surrounding conditions. The variations in the 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 enclosed in a glass container as shown in Fig. 1. This allowed the apparatus to be evacuated or sealed off as desired in order to preserve a constant atmospheric condition. A solenoid with an iron plunger connected to a glass rod was used to apply pressure to the

crystal, which was mounted on a hard rubber block directly below.   The
weight of the plunger and the effect of residual magnetism were com-
pensated by a spring and screw attachment which could be adjusted
from the outside by means of a ground glass tap.   To provide for a uni-
form application of force, the end of the glass rod was furnished with a
universal joint arrangement of hard rubber which came into contact with
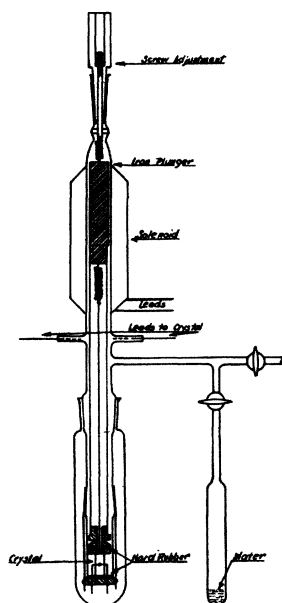

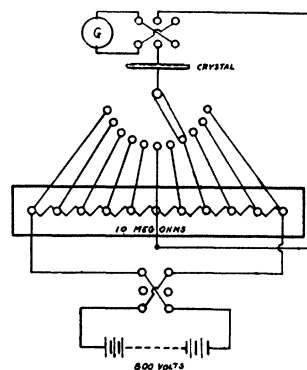Fig. 1.   Fig. 2.

the upper end of the crystal plate.   The crystal itself was supported on a
hard rubber block which was attached by metal strips to an inverted
cone.   This cone was clamped by a sleeve to a projection on a glass tube
as shown in the figure.

For regulating the humidity a bulb containing some water was con-
nected to the glass container.   During most of the experiments this bulb
was kept packed in ice, 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 means for the regulation of temperature by water baths
and freezing mixtures.   The temperatures were measured by copper-
constantan thermocouples whose junctions were soldered to the tinfoil
electrodes on the two faces of the crystal.   Two of the thermocouple
wires also served as connections to the ballistic galvanometer and to the
high voltage potentiometer 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. 2. The electromotive force usually employed was 800 volts, so that the potential applied was varied from $-$ 400 to $+$ 400 volts in steps of 80 volts each. The potentials used were measured by an electrostatic voltmeter.

The crystal plates were cut from a 100-gram crystal of Rochelle salt which was kindly furnished by Dr. Whitney, of the General Electric Company, to whom the writer wishes to express his appreciation. The plates were cut in the manner described by Cady, namely by a wet thread operating over two pulleys and kept moist by running through some water. The faces were dressed down and smoothened by a moist piece of ground glass. The orientation was such as to give the maximum response. The faces were accordingly perpendicular to the $\bar{a}$ axis of the crystal, the edges making angles of 45° with the $\bar{b}$ and $\bar{c}$ axes. A compression of the ends of the slab so cut results in a shear in the bc directions. Such a shear produces a maximum of piezo-electric polarization in the direction at right angles to its plane. Denoting the polarization by p_1 and the shear by Y_z we have according to Voigt[1] $p_1 = -\delta_{14}Y_z$. The charge q on a crystal of length l, breadth b, and thickness d, will be: $q = -\delta_{14}F(l/2d)$, where F is the total force on the end of the crystal. The piezo-electric modulus δ_{14} here concerned may have any value between practically zero and about 40×10^{11} e.s.u./dyne. It varies in a capricious manner in response to a number of conditions such as temperature, humidity, and previous history as to electrical and mechanical treatment. These latter fatigue effects, described by Cady,[2] are not permanent but persist often for many hours. The effect of humidity is to make the response greater. Preliminary observations seem to indicate that for changes in temperature the response is small above 35° or 40° C. and that it increases as the temperature is lowered, rising to a maximum at about 0° C. and then slowly decreasing again.

Investigating the behavior of the crystal as a condenser, the conclusions as to a hysteresis in D were verified, the method being that given by Ewing.[3] The hysteresis loops were unsymmetrical as was to be expected if the crystal had a natural polarization. The exact nature of the loops varied with the moisture and temperature conditions. Fig. 3 shows the results of observations taken at a temperature of 23° C. and a relative humidity of 30 per cent. Fig. 4 shows a loop obtained at 0° C., with the

[1] W. Voigt, Lehrbuch der Krystalphysik, p. 818.

[2] W. G. Cady, Report to National Research Council, May, 1918.

[3] Ewing, Magnetic Induction in Iron and other Metals, pp. 358–60.

surfaces of the crystal thoroughly dried.   The plate had been kept under cover with P_2O_5 for 15 hours before these observations were made. After 24 more hours under these conditions there was, however, very little hysteresis and only a very small piezo-electric activity, apparently due to the excessive dryness.   The moment per unit volume in the natural state varies but is of the order of 50 e.s.u./cm.^{2} under ordinary conditions·
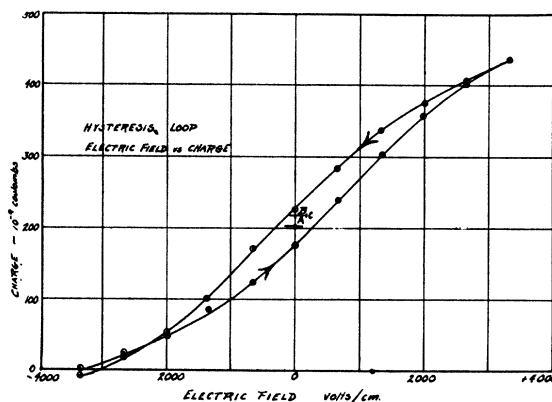

Fig. 3.

It was also observed that the response to pressure underwent a hysteresis with respect to changes in the temperature when the absolute humidity was kept constant by the method described.   This hysteresis accordingly may be partly or wholly due to slow changes in the moisture content at the various temperatures concerned.   Further work on this point is under way.   That such variations in moisture held by the crystal
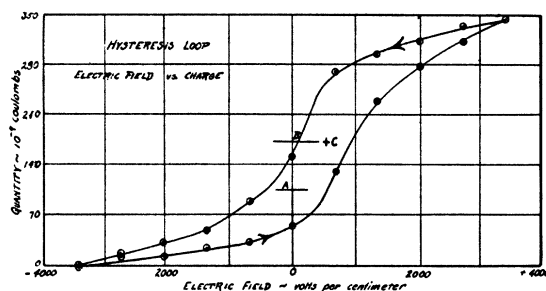

Fig. 4.

actually occur was shown by periodic weighing of two crystal plates which were kept respectively under moist and dry conditions.   The changes in weight during the first four days amounted to 5 per cent.

Curves showing the relation between electric field and piezo-electric

response were obtained for a number of values of the applied force (Fig. 5). All of the curves show a maximum for an applied steady field of a certain sign, while they fall off gradually in the opposite direction. These curves may be qualitatively explained on the basis of the hysteresis loops already discussed. It is quite obvious that the change in electric moment, which is the quantity measured, depends on crystalline strain.
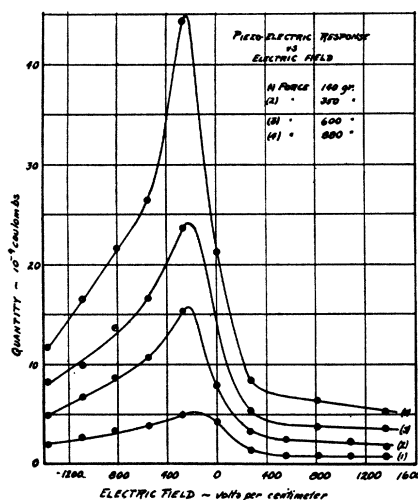

Fig. 5.

Since an electric field produces a piezo-electric stress, one may expect that a mechanical force applied on top of this field is equivalent to a certain extent to a change in applied field. If this equivalence were strictly so, the curves obtained would be just the derivatives of a branch of the hysteresis loop, namely dD/dE versus E. The similarity is apparent, and it is seen moreover, that the curves of Fig. 5 are analogous to the susceptibility curves in the case of magnetism.

Anderson[1] has obtained a set of curves somewhat similar in character by observations made on the charge and discharge of a crystal condenser when under pressure. These results may likewise be attributed to the equivalence of force and electric field in producing a change in the piezo-electric moment. Here, however, the curves are derived from the relation of D and F, which is very much like that of D and E considered above.

The center C of the loop is found by a consideration of symmetry, and may be assumed to represent the condition of no polarization. If the natural condition of polarization is assumed to lie half-way between the two branches of the loop at zero field, then the value of the perma-

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[1] J. A. Anderson, Reports to the National Research Council, March and April, 1918.

nent polarization is given by AB, Figs. 3 and 4. Values so obtained give 16 e.s.u./cm.^{2} and 85 e.s.u./cm.^{2} in the two cases respectively. Using 282.2 as the molecular weight of Rochelle salt, 1.76 as its density, and 1.66×10^{-24} grams as the mass of the Hydrogen atom, it follows that there are 3.76×10^{21} molecules per cubic centimeter. The corresponding molecular moments are then 4.26×10^{-21} e.s.u. and 22.6×10^{-21} e.s.u. respectively. If it is assumed that only one electron takes part in the creation of the natural polarization, the moment arm becomes equal to 8.9×10^{-12} cm. and 24.7×10^{-11} cm. in the two cases mentioned above, or at least one thousandth of the diameter of the hydrogen atom. The number of electrons in each molecule may, however, be taken as the sum of the atomic numbers of the elements involved ($NaKC_4H_4O_6 \cdot 6H_2O$) giving a value of 140. These may be equally affected in the natural condition of the crystal, which would indicate a separation of 6.4×10^{-14} cm. and 3.4×10^{-13} cm. respectively, which is the order of the diameter of the electron.

The writer takes this opportunity to thank Professor W. F. G. Swann for his continued interest in this research.

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    December 4, 1920.