DIELECTRIC ANOMALIES IN ROCHELLE SALT CRYSTALS

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ABSTRACT

Residual charge and fatigue effects for Rochelle salt condenser.—The throw of a ballistic galvanometer connected to a condenser with Rochelle salt crystal as dielectric depends on the time of charging and the time of discharging. It increases to a maximum as the charging time is increased to 2 sec. (for crystal plates .15 cm. thick) and then decreases slowly, reaching for a time of 24 hours a value about half the original. The decrease of the throw for .03 sec. charging, due to fatiguing for 24 hours at 100 volts, was found to be nearly independent of the temperature from −15°C to +20°C. The first increase is probably due to residual charges which are easily displaced to a more or less definite limit and which account for the high dielectric constant in this temperature range. The subsequent decrease is due to a fatigue effect which may be likened to an electrolytic polarization of the internal displacement current. These effects are associated with the water of crystallization, since dessication decreases them while previous soaking in alcohol accelerates them. To explain the limited temperature range of the effects it is supposed that at −20°C there is a loosening of the water ions enough to permit a slight motion of about 10^{-9} cm with reference to the Rochelle salt molecules, while at temperatures above +25°C further loosening allows electrolytic conduction to increase greatly.

Thermal changes in Rochelle salt.—There is apparently an evolution of heat starting at 24°C and persisting to 54°C where a very strong absorption of heat takes place.

ROCHELLE salt crystals have some unusual dielectric properties between −20°C and +25°C, that is, in the range of greatest piezoelectric activity. Many of these have already been described.[1] For example, at 0°C the specific inductive capacity for the ă crystallographic direction apparently reaches the extremely high value of 800 as determined by measurements of the ordinary charge by a ballistic galvanometer. If the discharging time is limited to 0.03 sec. by means of a Helmholtz pendulum, this value is reduced to 700. If, again, measurements are made with an oscillating circuit at two million cycles the dielectric constant is, according to Frayne,[2] about 80. The high values at low frequency are not due to ordinary conduction because this is much too small below 30°C to give over 0.1 percent of the total charge. In this connection it is also significant that the specific inductive capacity *decreases* between 25°C and 30°C, while the conductivity as measured by an electrometer shows a ten-fold *increase*. The explanation is rather

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[1] Valasek, Phys. Rev. **17,** 475 (1921) and **19,** 478 (1922)

[2] Frayne, Phys. Rev. **21,** 348 (1923)

that the residual charge and the internal conduction effects are very large, contributing up to 90 percent of the total dielectric constant at low frequencies.

There are several theories to explain residual charges. Maxwell[3] has suggested a non-uniform, layered dielectric. Von Schweidler[4] has suggested two theories, one of them based on motion of ions as in a very dense gas, and the other on the assumption of over-damped bound charges. A very successful approach to the subject of residual charge, leading to satisfactory equations but to no definite picture of the mechanism, is through analogy with residual elasticity.[5]

All these theories lead to the conception of a residual charge current which flows for some time whenever there is a change in the potential difference between the plates of the condenser. The integral of this current over the time of charge or discharge gives the quantity to be added to the corresponding "free" charge. A very important conclusion about the manner of variation of the residual charge current, which has been the object of much experimentation, is the so-called "super-position principle" of Hopkinson.[6] It states that any variation in the electric field produces a variation in the anomalous current which is independent of the field or the dielectric displacement already existing. This principle will now be applied to the special case where the variation in the field is equal to the field itself, namely in simple discharging of the condenser.

Let $f(t)$ represent the residual charge current while the condenser is being charged. This is some monotonically decreasing function probably the sum of two or three exponentials.[7] Let the time of charging be t_1 and let the instant of discharging be the time origin. The residual current on charging, if continued, would be $f(t_1+t)$. The change in voltage being equal and opposite to the charging voltage, there will be superposed on this current, one equal to $-f(t)$. The residual charge current on discharge will therefore be equal to $-f(t)+f(t_1+t)$. Now if δ is the time that this current flows through the galvanometer, the discharge will be greater by the integral of this current from zero to δ. That is, if R is the contribution of the residual charge current to the discharge, then (calling the current positive) it follows that

$$R=\int_0^\delta [f(t)-f(t_1+t)]dt=F(t_1\,,\,\delta) \tag{1}$$

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[3] Maxwell, Electricity and Magnetism, I, §§ 328-330.

[4] Von Schweidler, Ann. der Phys. **24,** 711 (1907)

[5] Wagner, Ann. der Phys. (4), **40,** 817 (1913)

[6] Hopkinson, Phil. Trans. **167,** 599 (1877)

[7] Jaquerod and Mugeli, Arch. des Sci. **4,** 10 (1922)

Now since $f(t)$ is monotonically decreasing, it follows that R must increase for increases in either δ or t_1. The first conclusion is easily verified experimentally with Rochelle salt, for the residual charge effect is very large and accounts for the difference between the ordinary specific inductive capacity and that obtained with short charging times or high frequencies.

The conclusion that R increases with t_1 is, however, not found to hold for charging times greater than several seconds. When the time of charging is increased beyond this, the discharge is found to become much smaller. This may be supposed due to a fatigue of the dielectric. While the crystal is being fatigued by the application of a field of a certain sign, one finds on reversing the field for a moment that the total discharge as well as the part due to residual charge increases for this opposite direction of charging. This effect has been observed only between $-20°C$ and $+25°C$ where the crystal is piezo-electrically active.

The object of this article is to describe experiments on these dielectric anomalies and to show their relationship to each other and to the piezo-electric effect.

Experimental Procedure

The crystal plates were all cut from a large perfect crystal which was kindly furnished by W. R. Whitney of the General Electric Company. The faces were in most cases perpendicular to the $\breve{a}$ crystallographic axis since in this direction the effects it was proposed to study are the greatest. The plates were usually about 0.15 cm thick, the electrode area being about 2 cm^2. After considerable experimentation it was found that amalgamated tinfoil electrodes squeegeed on polished surfaces of the crystal gave the most constant results. The crystal plates used were not dessicated or otherwise treated unless specifically stated, the electrodes being usually attached to the clear crystal immediately after polishing on a ground glass. While the observations were being made the crystal was kept in an air-tight tube containing KOH. This proved to be the most satisfactory arrangement for eliminating electrical leakage due to moisture without causing dehydration of the crystal.

The tube containing the crystal was immersed in a Dewar flask in order that the observations could be taken at various constant temperatures. The charging and discharging throws of the crystal condenser were measured by means of a Leeds and Northrup high sensitivity ballistic galvanometer. The times of charging and discharging were controlled by means of a set of switches operated by a Helmholtz pendulum. The apparatus was calibrated by means of a standardized Gerdien air condenser which could be substituted by opening the tube without changing any of the external connections.

Dielectric Fatigue

Below −20°C and above +25°C Rochelle salt has quite normal electrical properties, the hysteresis[8] vanishing and the other anomalies not being unusual. Between −20°C and +25°C the dielectric properties show peculiarities and the crystal is piezo-electrically active. In this temperature interval the dielectric constant is very large, as though a new type of polarization were created at −20°C, causing the increase in the dielectric constant and being responsible for practically the entire piezo-electric effect.

The polarization produced by these loosely bound charges appears to be rather sluggish in response to any field or force which may be applied to the crystal. This is the residual charge effect, the discharges of the condenser becoming larger when longer times of discharging are used. When, however, the time of *charging* is made longer, the discharges for a constant time of discharging become smaller for charging times greater than about one second in case of a plate which has been in alcohol for two days. This is the fatigue effect. Untreated crystals also show fatigue but it does not appear as soon. Observations of these effects are given in Table I.

Table I

Observations showing residual charge and fatigue effects

Discharging time 0.03 sec.; temp. 20°C; field 900 v/cm.

Charging time	Discharge (untreated)	Discharge (alc. 2 days)
0.03 sec	2.15	3.12
0.15	2.34	3.51
0.50	2.46	3.55
2.0	2.49	3.43
6.0	2.48	3.29
30	2.50	3.04
180	2.47	2.70
1200	2.33	2.25
3600	——	2.00
5800	1.94	——

For short times of charging the discharges are seen to increase as they should according to the superposition principle. The smaller discharges for the longer times of charging are attributed to a dielectric fatigue which is related to the internal conduction.

When fields of 900 or 1000 v/cm are applied for several hours, the discharges of the condenser are reduced by an amount which depends on the fatigue already existing. In order to know the exact state of the

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[8] Valasek, Phys. Rev. **19**, 479 (1922)

fatigue, it is best to apply a potential (e.g. 100 volts) for at least 24 hours before making any observations. The fatigue is then definite and the results are reproducible.

A fatigue of this kind is found to diminish the discharge $\Delta\sigma$ for the same direction of charging and to increase it for discharges from the opposite direction. If now the opposite field $-E$ is applied for an increasing time t, there is recovery of the low values and a decrease of the high values in an approximately exponential manner. These results are illustrated by Fig. 1.

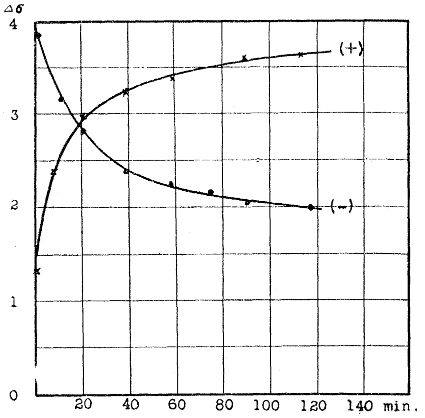

Fig. 1. Fatigue and recovery of Rochelle salt condenser after charging for 24 hr with +100 volts, then applying−100 volts.

It is interesting to note that if one compares the fatigued values of the discharges for various short increasing discharging times it is found that the positive and negative values are nearly proportionately increased. This is illustrated by Table II, where the negative discharge is over twice the positive due to fatigue, yet the ratios of the discharges for 0.03 and for 1 sec are nearly the same. This shows that the residual charge effect is the same in both cases.

TABLE II

Charging time 10 hours

Discharging time	+Discharge	−Discharge	Ratio
0.03 sec	1.63	3.54	2.17
0.08	1.67	3.60	2.16
0.17	1.71	3.72	2.18
0.48	1.76	3.90	2.22
1.0	1.88	4.12	2.19

The hysteresis loop of the charge σ and the field E is a fatigue effect of the kind described above. The observations are taken by a method analogous to one described by Ewing[9] for obtaining magnetic hysteresis loops. Each observation of $\Delta\sigma$ is taken after a number of reversals in the field, by making the final change of ΔE from either the $+E$ or the $-E$ reached on the last reversal, with the crystal connected across the galvanometer. The value of ΔE is increased until it amounts to an entire reversal. The short time that the maximum field is applied just before the measurements are made fatigues the crystal and it does not return to the normal state on discharge but recovers gradually at a rate depending on the field and the time of application. The hysteresis loop can thus be made larger by taking the observations after a longer pause at the maximum fields. These effects are greatest when the crystal is treated with alcohol.

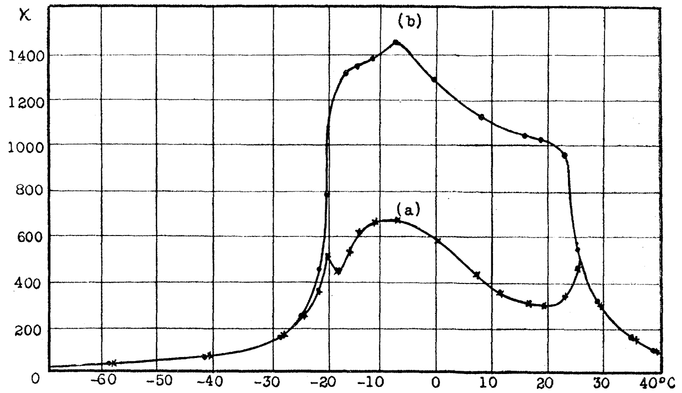

Fig. 2. Temperature variation of fatigue after charging for 24 hr with + 100 volts. Average dielectric constants for discharges (a) from + 100 and (b) from − 100 volts, for a discharging time of .03 sec.

Fatigue is observed only at temperatures between −20°C and +25°C and it is clearly related to the fatigue one observes in the piezo-electric response. The variation with temperature is illustrated in Fig. 2. The observations were taken after the crystal had been fatigued for 24 hours at +100 volts. The average rate of heating was about ten degrees per hour. The ordinates for curves (a) and (b) represent the average dielectric constants for discharges from +100 and −100 volts respectively and for a discharging time of 0.03 sec. Between −15°C and +20°C the two curves are approximately parallel, showing that the change in the dielectric constant due to fatigue is independent of temperature in this range. Besides the differences in the heights of the two curves, one notices the

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[9] Ewing, Magnetic Induction, 358.

peaks at $-20°C$ and at $+25°C$ on one of them.[10] These are only observed when the time of charging is short, fatigue tending to make them more pronounced. They show the appearance of the type of variation of specific inductive capacity that Frayne[11] observed at high frequencies. At optical frequencies there are no peculiar variations in the indices of refraction of the crystal at these temperatures.[12]

Internal Conduction

The nature of the relation between the polarization and the field, as well as the very high dielectric constant of Rochelle salt, indicates the presence of charges which are in a sense intermediate between the ordinary bound and free charges. They are easily displaced to a more or less well defined limit beyond which the displacement becomes difficult. The internal currents produced by them are restricted to small regions inside the crystal. A distinction between this internal conduction and the actual conduction is shown most strikingly above $+25°C$ where the actual conduction increases exponentially with the temperature, while the abnormally high dielectric constant due to internal conduction decreases. The fatigue effect may be likened to an electrolytic polarization of the internal current which is probably confined to the Rochelle salt molecule and is perhaps due to the water of crystallization.

Among the reasons for attributing the internal conduction to the water of crystallization is the fact that when the crystal is dehydrated by means of phosphorus pentoxide, the high dielectric constant is greatly reduced, and with complete dessication there are no longer any transitions at $-20°C$ and $+25°C$. The conductivity increases with temperature but not as rapidly as before.

After the crystal has been immersed in alcohol, different effects are observed. The piezo-electric activity is fully six times as great as before. The specific inductive capacity is also increased but not in as great a proportion. Even by the use of tinfoil electrodes attached by means of shellac dissolved in alcohol, the capacity deflections may be doubled or tripled. These deflections decrease after the shellac dries but there is some permanent improvement. The effect of alcohol can be best studied by using amalgamated tinfoil electrodes since they can be readily stripped off and attached again in exactly the same way after the crystal has been

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[10] These maxima are very different in origin from the second maximum noted by the writer (Phys. Rev. **19**, 485, 1922) which was merely due to the improvement of an imperfect contact when the conductivity of the crystal increased.

[11] Frayne, Phys. Rev. **21**, 355 (1923)

[12] Valasek, Phys. Rev. **20**, 644 (1922)

kept in alcohol for a time. After two days immersion the capacity deflections are about doubled for the ordinary charges (1 sec. discharging time for example), the discharges not being changed as much for shorter times. This is for the unfatigued crystal. Fatigue causes a change in the relative increases of the discharges for the two directions and discharging times. The results are shown in Table III which also shows the relative persistence of the effects.

TABLE III

	+Discharge		−Discharge	
	03 sec.	1 sec.	.03 sec.	1 sec.
Untreated	1.63	1.88	3.54	4.15
Alcohol 2 days	1.83	4.60	7.08	12.10
2 days later	2.11	4.07	7.70	11.10
24 days later	2.22	3.69	5.85	8.08

The observations in the table are all taken after an application of +90 volts for 24 hours. Accordingly the values in the columns headed + are smaller and those headed − are larger than normal, due to fatigue. Two discharging times are used, namely 0.03 and 1 second in order to indicate the magnitude of the residual charge effect. A comparison of these will show that the residual charges are greatly increased by the alcohol; in fact, the increase in specific inductive capacity seems to be wholly due to increased residual charges. The relative amount of fatigue is also increased, showing that alcohol affects whatever is responsible for the anomalous dielectric action of Rochelle salt, this being most probably the water of crystallization.

In order to test for the presence of electrolytic polarization layers or space charges, a platinum wire probe was sealed into the crystal, one third the distance from one of the plates, and connected to a string electrometer. Unless the temperature was very steady for at least an hour a potential difference of several volts was indicated even though the plates were earthed. This was due to the so-called "false" pyro-electric effect resulting from the thermo-elastic stresses set up by temperature gradients in the crystal. The resulting internal potentials produced fatigue effects. Perhaps the variations that have been observed in the dielectric anomalies of quartz and other crystals may be due to such effects.

The probe measurements showed that there are no unsymmetrical polarization layers in Rochelle salt. There is, however, a symmetrical variation from a linear potential drop through the crystal. It is not known whether there are equal potential jumps at both plates or a continuous variation in potential as in quartz.[13]

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[13] Joffe, Ann. der Phys. 72, 4 (1924)

It would be of interest to inquire whether it is possible to account for the high dielectric constant of Rochelle salt on the basis of the water of crystallization without requiring greater displacements of the ions than the distances between molecules. To do this one must know the maximum polarization. The polarization gradually approaches saturation which is, however, never reached because the crystal breaks when the field exceeds about 25,000 volts per centimeter. The maximum polarization obtainable is less than 15,000 e.s.u./cm^3. There are four molecules of water for every molecule of Rochelle salt. In a crystal lattice, each molecule of water may be regarded as equivalent to three ions, two H^+ and one O^{--}. Suppose that the restoring force per unit displacement per unit charge is the same, then $P_{max} = 16\ Ne\xi_{max}$, where P is the polarization, e is the electronic charge, and ξ is the displacement. From the density and molecular weight of Rochelle salt and the mass of the hydrogen atom, it is found that there are $N = 3.76 \times 10^{21}$ molecules per cubic centimeter. From this value of N one finds that the average distance between molecules is 3×10^{-7} cm, whereas the formula above gives $\xi_{max} = 5 \times 10^{-10}$ cm. There is accordingly no contradiction with the assumption that the water of crystallization furnishes the ions for the internal conduction and that these ions do not move out of the molecule.

With reference to the possible interpretations of the critical temperatures of $-20°$ and $+25°$C it has been said that the former is the temperature at which the ions of the water of crystallization are loosened sufficiently to give rise to internal conduction. The temperature may be called in one sense a melting point of the water of crystallization. However, it was not possible to detect any absorption of heat at this point with a sensitive differential thermocouple. Above $+25°$C the internal conduction ions are gradually freed so that they may migrate through the crystal; the conduction increases approximately in an exponential manner until at $+54°$C the crystal goes through a transition point and is converted into a moist granular mixture of the single tartrates of sodium and potassium with water. A differential thermocouple indicates an apparent evolution of heat starting at $+24°$C and persisting to $+54°$C where a very strong absorption of heat takes place.

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