fluid system. The results are in excellent agreement with experiment. Minor discrepancies may well be due to small inaccuracies in the caloric measurements, although the theory will have to be refined to include small effects neglected at present, like dissipation and the dependence of ρ_n/ρ on pressure. The formalism developed seems to furnish valuable criteria for the consistency of measurements and might possibly be used to establish the thermodynamic temperature scale.

The principal problems for further experimental and theoretical research seem to be as follows:

(1) The derivation of the postulates of the quasi-thermodynamic theory from first principles. In particular, establishing the correct molecular model which would lead to these postulates. At present the choice seems to be between the Bose-Einstein liquid and possibly the vortex model (modified Landau theory). The experimental approach to this problem has been briefly discussed at the end of Section VI.

(2) *The clarification of the nature of the pure superfluid liquid* (*helium II near absolute zero*). This problem has not been discussed in the present paper. According to Landau, the superfluid state is characterized by the condition $\text{curl}\mathbf{v}_s=0$. The question has been further discussed by F. London[18] and by Onsager.[35] So far, superfluidity (capillary flow and the creeping phenomenon) has been studied experimentally only above 1°K where the effects have been greatly complicated by the thermo-mechanical effect and the viscosity of the normal component. Experiments below 1°K where these effects practically vanish would be greatly desirable. Of particular interest is the investigation of the dissipation arising above the critical velocity. This seems to be of turbulent character; hence, a unique opportunity is offered for studying turbulence in the absence of viscosity (no boundary layer). On the other hand, this turbulence will be influenced by quantum effects.

The author wishes to extend his thanks to Dr. F. London for a long series of discussions extended over a period of years. They have led to the clarification of many of the questions considered in this paper. His thanks are also due Dr. Lars Onsager for stimulating discussions.

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[35] Private communication.

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Theory of the Ferroelectric Effect and Clamped Dielectric Constant of Rochelle Salt

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Using the crystal structure determination of rochelle salt made by Beevers and Hughes, a theory of the ferroelectric effect and clamped dielectric constant has been worked out using the displacement of the hydrogen nucleus in the 1–10 hydrogen bond as the ferroelectric dipole. This theory has only one disposable constant, β, the factor of proportionality between the polarization and the Lorentz internal field. Taking the oxygen separation found by x-rays, the dielectric constant for electrons and atoms found by experiment, and the number of molecules per cubic centimeter found from the x-ray cell determinations, the value of β becomes 4.07 which agrees well with the theoretical value $4\pi/3$ for an isotropic substance. This theory accounts for the clamped dielectric constant at low field strengths, which as shown by measurements presented here, has maximum values at −18°C and +24°C, the Curie temperatures for the free crystal. This shows that the anomaly must lie in the clamped dielectric constant alone and not in the interaction of the clamped dielectric constant and the piezoelectric effect. This model also accounts for recent measurements of W. A. Yager which show that the dipole dielectric constant is relaxed at a frequency of about 5×10^9 cycles.

I. INTRODUCTION

All measurements of the properties of rochelle salt indicate that the piezoelectric and elastic properties are normal and that all the anomalies reside in the "clamped" dielectric constant, i.e., the dielectric constant measured in the absence of strain. The piezoelectric stress has been found to be directly proportional to the

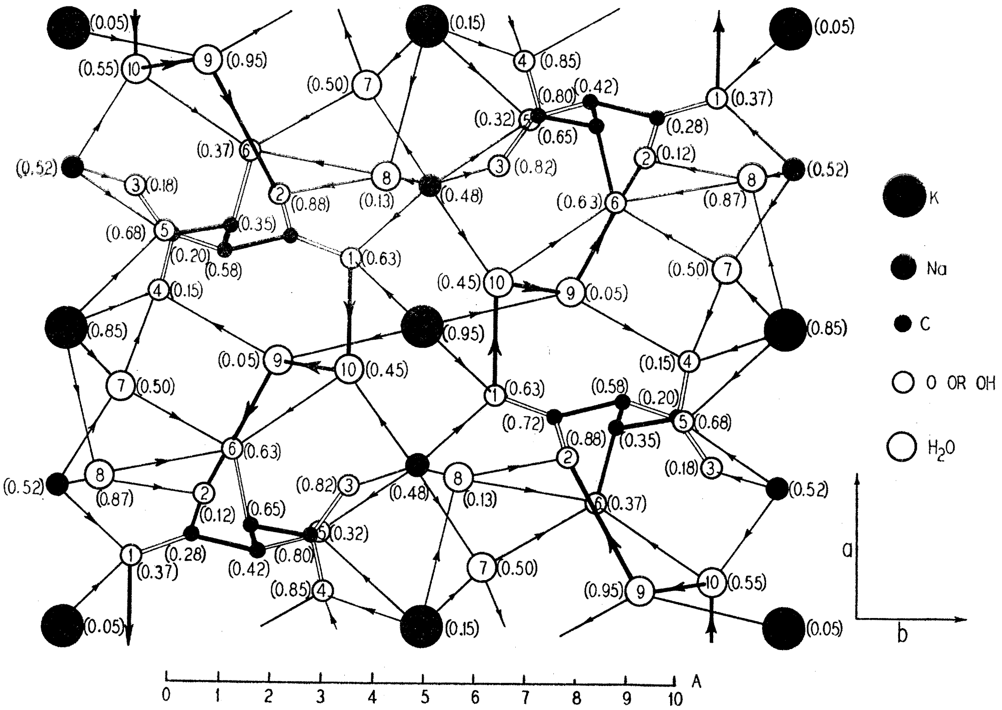

FIG. 1. Projection of (001) plane, of the structure of rochelle salt. The bonds involved in the 1–2–9–10 chains are drawn thick, so that the chains can be picked out.

Table of Coordinates

	$X=a$	$Y=b$	$Z=c$		$X=a$	$Y=b$	$Z=c$
2K on (*a*)	0.00	0.00	0.05	$4H_2O$ on (7)	0.40	0.08	0.50
2K on (*b*)	0.00	0.50	0.15	$4H_2O$ on (8)	0.25	0.05	0.87
4Na on	0.23	0.99	0.52	$4H_2O$ on (9)	0.44	0.30	0.05
4O on (1)	0.12	0.10	0.37	$4H_2O$ on (10)	0.42	0.40	0.45
4O on (2)	0.22	0.20	0.12	4C on	0.15	0.18	0.28
4O on (3)	0.23	0.40	0.82	4C on	0.12	0.28	0.42
4O on (4)	0.06	0.37	0.85	4C on	0.17	0.27	0.65
4OH on (5)	0.16	0.36	0.32	4C on	0.15	0.35	0.80
4OH on (6)	0.29	0.24	0.63				

dipole polarization and the large piezoelectric strain for rochelle salt is due to the large polarization for a given voltage, caused by the large clamped dielectric constant. Hence all theories of the ferroelectric effect in rochelle salt are primarily theories[1] of the clamped dielectric constant. The most recent and comprehensive of these theories is the interaction theory of Mueller,[2] which ascribes the spontaneous polarization between the Curie temperatures of −18°C and +24°C to an interaction between the clamped dielectric constant and the piezoelectric effect, which produces a unity electromechanical coupling between the mechanical displacement and the applied electric field when the clamped dielectric constant is high enough. This theory would indicate that the "monoclinally clamped" dielectric constant, i.e., the dielectric constant measured when the spontaneous polarization occurs but the frequency is so high that no piezoelectric motion can occur, would have Curie temperatures of −12°C and +18°C, i.e., well inside of the temperatures −18°C and +24°C. This is a prediction that can be tested experi-

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[1] W. G. Cady, a review of the theories of rochelle salt is given in *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

[2] H. Mueller, Phys. Rev. **57**, 829 (1940); *ibid.* Phys. Rev. **58**, 565 (1940).

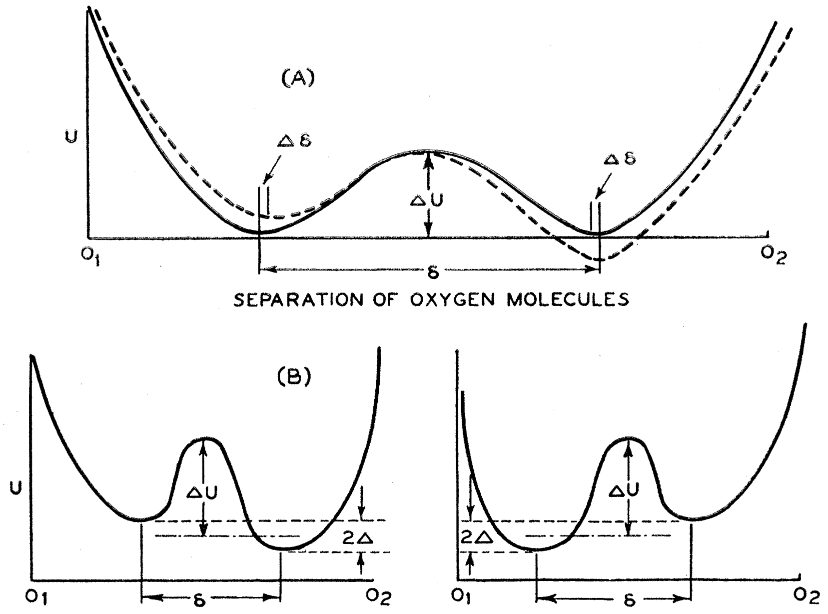

FIG. 2. Possible potential well distributions on 1–10 bond. (A) Potential well distribution if 1 and 10 are equivalent. (B) Potential well distributions if 1 and 10 are not equivalent.

mentally and measurements presented in this paper, made at 20 megacycles for large-sized crystals, do not show any displacement of the Curie temperatures from −18°C and +24°C. Hence the anomoly cannot reside in the interaction between the piezoelectric effect and the clamped dielectric constant but must reside in the clamped dielectric constant alone.

Recently, a determination of the crystal structure of rochelle salt has been made by Beevers and Hughes,[3] which indicates that the dipole causing the ferroelectric effect is one associated with the motion of a hydrogen nucleus along a hydrogen bond. The structure of rochelle salt according to Beevers and Hughes is shown by Fig. 1. There are three possible hydrogen bonds in the structure, between the oxygen molecule 1 and the water molecule 10, between the water molecule 10 and the water molecule 9, and between the water molecule 9 and the oxygen 2. The distances between the successive molecules are: 1 to 10 is 2.59A;[4] 9 to 10 is 2.86a; and 9 to 2 is 3.02A. The bond with the shortest distance is 1 to 10 (2.59A) and is believed by Beevers and Hughes and also by Ubbelohde and Woodward,[5] to be the dipole responsible for the ferroelectric properties of rochelle salt. This bond lies nearly along the X axis (X coordinate$=2.35$A; Y coordinate$=0$; Z coordinate$=\pm 1.09$A) which is the ferroelectric axis of the crystal. It is the purpose of this paper to discuss a theory based on the action of this hydrogen bond, which leads to a ferroelectric effect having the right value of spontaneous polarization, two Curie temperatures, a good quantitative agreement with the measured values of the clamped dielectric constant and agrees well with recent measurements of W. A. Yager on the dielectric constant of rochelle salt at a frequency of 2.5×10^{10} cycles, which show that the dipole dielectric constant is relaxed at a frequency of about 5×10^{9} cycles. No phenomenological constants are required and only one disposable constant is required, namely, β which is the factor of proportionality between the polarization and the Lorentz internal field.

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[3] C. A. Beevers and W. Hughes, Proc. Roy. Soc. **A177**, 251 (1941).

[4] The distance 1–10 calculated from Fig. 1 is 2.64A; but Ubbelohde and Woodward report that the most probable distance is 2.59±0.05A.

[5] A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc., **A185**, 448, 465 (1946). They suggest that the lower Curie point is caused by the disappearance of the two potential wells in the hydrogen bond. This cannot be true, for as shown in this paper such a disappearance would eliminate the temperature variable dipole below the lower Curie point and the measured dielectric constant should be independent of temperature. This does not agree with experiment.

II. FERROELECTRIC EFFECT IN ROCHELLE SALT

We suppose that in the undisturbed state, the hydrogen nucleus in the hydrogen bond 1 to 10, which lies at an angle of about 25° with the X axis of the crystal, is in the potential field shown by Fig. 2A. There are two minima, a potential barrier ΔU between them and a distance δ separating the two minima. Now according to elementary kinetic theory, the probability of a nucleus in one potential well jumping to the other potential well, per unit of time, is

$$\alpha=\Gamma e^{-\Delta U/kT}, \tag{1}$$

where Γ is a constant. (In Eyring's reaction rate theory $\Gamma=kT/h$.) Let α_+ be the probability of a particle jumping in the positive direction per unit of time and α_- be the probability of its jumping in the negative direction, and let N_+ be the population in the wells along the positive direction and N_- the population in the wells in the negative direction. Then the dipole polarization is equal to

$$(N_+-N_-)\mu=P_d, \tag{2}$$

where μ is the dipole moment along the X axis of the bond and neighboring atoms. Since the bond is at an angle of 25° from the X axis $\mu=\mu_A\cos 25°$ where μ_A is the absolute value of the dipole along the bond. We have also

$$N_++N_-=N, \tag{3}$$

the total number of dipoles per unit volume.

The rate at which the dipole polarization changes with time is

$$dP_d/dt=[N_-\alpha_+-N_+\alpha_-]\mu, \tag{4}$$

or it is the number of molecules in the wells along the negative direction times their probability of jumping to the positive wells minus the reverse reaction, all multiplied by the dipole moment μ. Now suppose that we put on a field E. This will change the potential wells as shown by the dotted line of Fig. 2. There is a change $\Delta\delta$, in the position of the minima and a change in the potential barriers that the molecules have to surmount in order to reach the other potential minima. The change in the positions of the potential minima does not depend on temperature, and the polarization caused by it can be combined with that for atoms and electrons. The dipole polarization which is due to the passage of the hydrogen nuclei over the potential barriers is controlled by the barriers.

$$(\Delta U-\tfrac{1}{2}Ee\delta) \quad \text{and} \quad (\Delta U+\tfrac{1}{2}Ee\delta), \tag{5}$$

where E is the field, e the electronic charge and δ the separation of the two wells. When we establish a field E and change the polarization, there will be an internal field of the Lorentz type given by the equation

$$F=E+\beta P, \tag{6}$$

where β is $4\pi/3$ for an isotropic medium, but may differ from it for a crystal. The total polarization consists of a part P_E due to electrons and atoms, which includes the hydrogen potential well displacement polarization, and a part P_d due to hydrogen bond dipoles. The electronic and atomic polarization excited will be proportional to the local field F, so that

$$F=E+\beta[P_E+P_d]=E+\beta[\gamma F+P_d]$$

or

$$F=(E+\beta P_d)/(1-\beta\gamma) \tag{7}$$

where γ is the polarizability per unit volume due to all polarization except that of the hydrogen dipole. Hence α_+ and α_- then become, since δ lies at an angle of 25° with the applied field E_X,

$$\alpha_+=\Gamma\exp-\left[\Delta U-\frac{e\delta\cos(25°)}{2(1-\beta\gamma)}(E+\beta P_d)\right]/kT;$$

$$\alpha_-=\Gamma\exp-\left[\Delta U+\frac{e\delta\cos(25°)}{2(1-\beta\gamma)}(E+\beta P_d)\right]/kT.$$

Since $N_-=N-N_+$; $P_d=(2N_+-N)\mu$ and

$$dP_d/dt=\tfrac{1}{2}N\mu(\alpha_+-\alpha_-)-\tfrac{1}{2}P_d(\alpha_++\alpha_-) \tag{8}$$

TABLE I. Height of the potential barrier and distance of the H nucleus from the center of the bond as functions of the oxygen separation.

Length of bond in angstrom units	2.592	2.60	2.65	2.70	2.75	2.80
Height of potential barrier ΔU in calories per mole	0	15	314	975	1980	3310
Distance of H nucleus from center of bond in angstrom units ($\delta/2$)	0	0.058	0.157	0.217	0.265	0.308

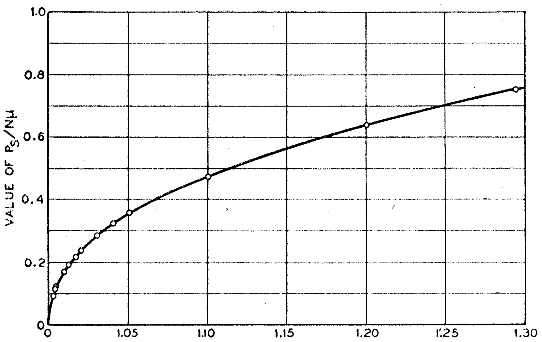

FIG. 3. Ratio of spontaneous polarization P_s to maximum dipole polarizations $N\mu$ as a function of A.

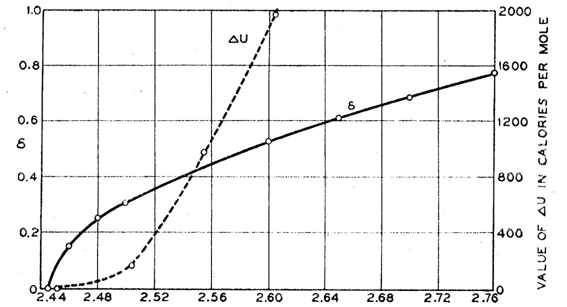

FIG. 4. Potential well separation δ and height of energy barrier ΔU as a function of the oxygen separation.

where μ is the dipole moment along the X axis, i.e., $\mu_A\cos(25°)$ where μ_A is the value of the dipole moment which lies in the direction of δ. Introducing the value of α_+ and α_- we have

$$\Gamma^{-1}e^{\Delta U/kT}\frac{dP_d}{dt}=N\mu\sinh\left[\frac{e\delta\cos(25°)}{2(1-\beta\gamma)kT}(E+\beta P_d)\right]-P_d\cosh\left[\frac{e\delta\cos(25°)}{2(1-\beta\gamma)kT}(E+\beta P_d)\right]. \quad (9)$$

This is the fundamental equation determining all the dielectric properties of the crystal. To simplify writing, we introduce the abbreviation

$$A=\frac{e\delta N\mu\beta\cos(25°)}{2(1-\beta\gamma)kT}=\frac{e\delta N\mu_A\beta\cos^2(25°)}{2(1-\beta\gamma)kT}, \quad (10)$$

so that Eq. (9) can be written in the form[6]

$$\Gamma^{-1}e^{\Delta U/kT}\frac{dP_d}{dt}=N\mu\sinh A\left[\frac{E}{\beta N\mu}+\frac{P_d}{N\mu}\right]-P_d\cosh A\left[\frac{E}{\beta N\mu}+\frac{P_d}{N\mu}\right]. \quad (11)$$

For static conditions where $dP/dt=0$, this becomes

$$\tanh A\left[\frac{E}{\beta N\mu}+\frac{P_d}{N\mu}\right]=P_d/N\mu. \quad (12)$$

Setting the field equal to zero, this equation becomes

$$P_d/N\mu=\tanh(AP_d/N\mu). \quad (13)$$

If the factor A is greater than unity, this equation will have positive and negative solutions other than zero, representing spontaneous polarization along the $+X$ or $-X$ direction. For values of A slightly greater than unity, we can replace $\tanh(AP_d/N\mu)$ by the first two terms of the expression or

$$(P_d/N\mu)=A(P_d/N\mu)-\tfrac{1}{3}A^3(P_d/N\mu)^3.$$

Solving for $P_d/N\mu$, we have

$$(P_d/N\mu)=(3(A-1)/A^3)^{\frac{1}{2}}. \quad (14)$$

A plot of this equation is given in Fig. 3.

For rochelle salt with cell dimensions 14.3A ×11.93A×6.17A, the unit cell has a volume of 1.05×10^{-21} cm^3. Since there are four dipoles per unit cell, the number N is 3.81×10^{21} dipoles per cm^3. If the hydrogen nucleus is midway between the two oxygens the bond is neutral and there is no dipole moment. Hence the value of the dipole moment should be given by the expression

$$\mu_A=\tfrac{1}{2}e\delta \quad (15)$$

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[6] It has been shown by J. M. Richardson that even if we regard the atoms 1 and 10 as not quite equivalent, which will divide the bonds into two sets having dissymetrical potential barriers along the X axis, as shown by Fig. 2B, the form of Eq. (11) is still the same. If the two barriers have potentials U_1 and U_2 equal to $U_1=U+\Delta$ and $U_2=U-\Delta$, the polarization P_d consists of two parts Pd_1 and Pd_2 given for static conditions by the equations

$$Pd_1/N\mu=\tanh\left[\frac{A}{\beta N\mu}(E+\beta P_d)+\frac{\Delta}{kT}\right]$$

and

$$Pd_2/N\mu=\tanh\left[\frac{A}{\beta N\mu}(E+\beta P_d)-\frac{\Delta}{kT}\right].$$

On expanding the polarization in a power series, we have:

$$P_d/N\mu=(Pd_1+Pd_2)/N\mu$$
$$=[1-(\Delta/kT)^2][AP_d/N\mu]-\tfrac{1}{3}A^3(P_d/N\mu)^3.$$

Since Δ/kT is a small quantity, this results practically in defining a new value of A equal to

$$A'=A[1-(\Delta/kT)^2].$$

and the expression for A becomes

$$A=e^2\delta^2\beta N\cos^2(25°)/4(1-\beta\gamma)kT. \tag{16}$$

In order to calculate A we have to know how the separation δ depends on the separation of the oxygens 1 and 10. Some idea of the change in δ can be had from a calculation of Huggins[7] on the shape of the potential curve for a free hydrogen bond. He finds that the shape of the curve depends on the oxygen separation. Table I shows the height of the potential barrier and the distance of the H nucleus from the center of the bond ($\delta/2$) as a function of the separation of the oxygens. Unfortunately, with the constants chosen, these data do not agree with the accepted values for water which, according to Pauling,[8] are a separation of 2.76A results in a value of $\delta=0.78$A. If we adjust the constants of Huggin's equation to give this value, the values of δ and ΔU are shown plotted on Fig. 4.

As an indication of the consistency of this theory, a calculation of the value of A is attempted at 297°K, the upper Curie point where A should be unity. From x-ray data, the value of the oxygen separation is 2.59 ± 0.05A. All the experimental data are found to be satisfied best if we take the separation as 2.57A, a value within the experimental error. With this value $\delta=0.4655$A. All the quantities of Eq. (16) are known except β and γ the polarizability. An estimate of these can be made as follows. The values of β and γ are related to the dielectric constant for electrons and atoms by the formula

$$(\epsilon_0-1)/[3+3\beta(\epsilon_0-1)/4\pi]=4\pi\gamma/3, \tag{17}$$

where ϵ_0 is the dielectric constant for electrons and atoms, i.e., due to all sources except the hydrogen bond dipoles. Since the index of refraction for rochelle salt along the X axis is 1.4954, the electronic dielectric constant is the square of this, or 2.24. At −160°C, the dielectric constant is 7.0. As discussed later, this dielectric constant, which is independent of temperature for temperatures lower than −160°C, is due to the electronic and atomic polarization plus a polarization due to the displacement of the hydrogen nuclei due to the change in the equlibrium position of a single potential well. For the double potential well of Fig. 2A, the polarization due to the displacement of the equilibrium positions will be half as large so that a value $\epsilon_0=6.0$ is assumed, which seems to be a reasonable value. Substituting in Eq. (17)

$$\gamma=1/(\tfrac{1}{5}4\pi+\beta). \tag{18}$$

Substituting all the known values in the expression for A, we have

$$A=\frac{(4.77\times10^{-10})^2(0.465\times10^{-8})^2\times3.81\times10^{21}\times0.819\beta}{4\times1.37\times10^{-16}\times297\left[\dfrac{4\pi/5}{4\pi/5+\beta}\right]}=1. \tag{19}$$

The only unknown is β and solving for this, $\beta=4.07$ which is very close to the theoretical value for an isotropic substance $4\pi/3=4.19$.

To calculate A over a temperature range, one would have to know how the separation of the oxygen atoms varied with temperature on which no data are available. However, since the hydrogen bond is the weakest bond in the structure, one would expect that a good share of the temperature expansion of the crystal would come across this bond. Measurements[9] of the temperature expansion along the X axis show that

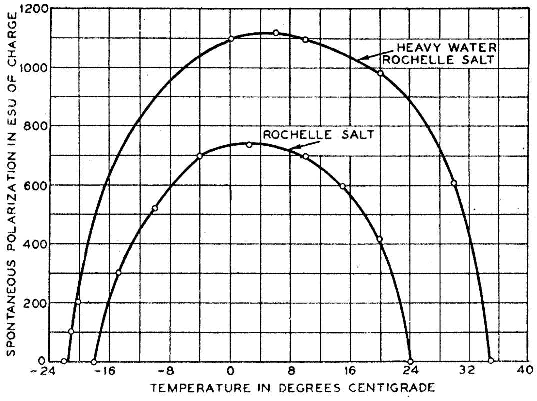

FIG. 5. Spontaneous polarization of rochelle salt and heavy water rochelle salt plotted as a function of temperature.

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[7] M. L. Huggins, J. Phys. Chem. **40**, 723 (1936).

[8] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), Chapter IX, plate 361.

[9] W. P. Mason, Bell Sys. Tech. J. **26**, No. 1 (1947).

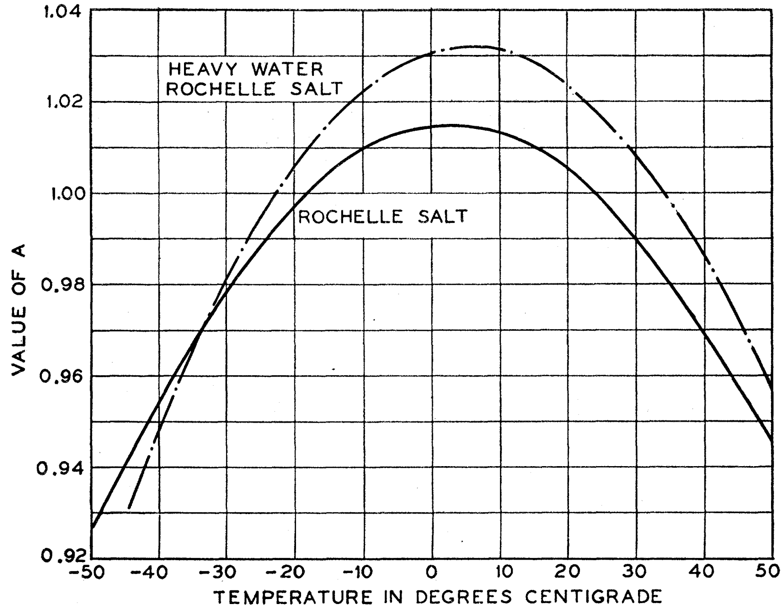

FIG. 6. Calculated value of A for rochelle salt and heavy water rochelle salt as a function of temperature.

from $-50°\mathrm{C}$ to $+40°\mathrm{C}$, the temperature expansion averages about 65×10^{-6} per degree C. Since the value of $A=1$ at $-18°\mathrm{C}$, the other Curie temperature, an estimate can be made of the proportion of the total expansion that comes across the hydrogen bond. The values of N, β, and γ will all vary slightly with temperature but their variations should be small compared to δ and hence it will be assumed that the complete variation occurs in δ. To obtain $A=1$ at $-18°\mathrm{C}$ requires a value of $\delta=0.431\mathrm{A}$. From Fig. 4 this corresponds to an oxygen separation of 2.5535A. This represents a decrease in separation of 0.0165A from 24°C to $-18°\mathrm{C}$. From the temperature expansion data the complete expansion of the unit cell of 11.93A along the X axis should be

$$65\times10^{-6}\times42\times11.93=0.0325\mathrm{A}. \tag{20}$$

Hence 51 percent of the total expansion occurs across the hydrogen bond, which appears to be a reasonable value.

Between $-18°\mathrm{C}$ and $+24°\mathrm{C}$ the value of A can be calculated from the experimental[10] values of the spontaneous polarization shown in Fig. 5. The ratio of the spontaneous polarization to the total dipole polarization is given by Eq. (14) and is plotted in Fig. 3. The total dipole polarization along the X axis at 24°C (297°K) is

$$N\mu=\tfrac{1}{2}Ne\delta\cos(25°)=\tfrac{1}{2}3.81\times10^{21}\times4.77\times10^{-10}\times0.4655\times10^{-8}\times0.904=3850\text{ esu.}$$

At $-18°\mathrm{C}$ (255°K), since δ has decreased to 0.431A, $N\mu=3550$ esu. Assuming that $N\mu$ is a straight line function of temperature between these points, the value of A can be calculated between $-18°\mathrm{C}$ and $+24°\mathrm{C}$ and is shown plotted on Fig. 6. It is very closely a parabola, and hence we can extend the values on either side of the Curie region as shown in Fig. 6. From the values of A, the values of δ can be calculated and from Fig. 4 the separation of the oxygens can be calculated. These are shown plotted on Fig. 7. If we extrapolate the curves to low temperatures it appears that a separation of 2.446A (the separation for which $\delta=0$ and the two potential wells disappear) will occur at about $-160°\mathrm{C}$. At this temperature, the temperature variable part of the dielectric constant should disappear. Some confirmation[11] of this calculation is found experimentally for at that temperature the dielectric constant is 7.0 and does not change as the temperature is lowered. Figure 7 indicates that the separations of the oxygens increases more slowly with temperature for temperatures

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[10] H. Mueller, Ann. Acad. Sci. N. Y. **40**, 338 (1940).

[11] See W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 559, Fig. 121.

above −30°C. This may be accounted for by the small mass of the hydrogen nucleus which acquires its full kinetic energy at a lower temperature than do the heavier molecules of the crystal. At the higher temperatures these other atoms acquire their full motion and hence the expansion along the hydrogen bond becomes less in proportion to the total expansion.

Equation (12) and the constants evaluated from the above consideration give methods for determining the properties of the crystal at large field strengths. This equation holds primarily for a single domain. Since $(A/\beta N\mu)$ has a value of 6.7×10^{-5} at 0°C, the hyperbolic tangent of Eq. (12) can be expanded into the form

$$\tanh A\left[\frac{E}{\beta N\mu}+\frac{P_d}{N\mu}\right]$$
$$\frac{\tanh(AE/\beta N\mu)+\tanh(AP_d/N\mu)}{1+\tanh(AE/\beta N\mu)\tanh(AP_d/N\mu)}$$
$$\doteq 6.7\times10^{-5}E+\tanh AP_d/N\mu. \quad (21)$$

Since $AP_d/N\mu$ is in the order of 0.20 at the largest, we can replace the hyperbolic tangent by the first two terms of its power series, and Eq. (21) can be written

$$(AP_d/N\mu)-\tfrac{1}{3}A^3(P_d/N\mu)^3$$
$$=-6.7\times10^{-5}E+P_d/N\mu. \quad (22)$$

If P_s is the solution for the spontaneous polarization when $E=0$, we can write

$$P_d=P_s+\Delta P.$$

Solving for ΔP, we find

$$\Delta P=(AE/\beta)/[A^3(P_s/N\mu)^2-(A-1)]. \quad (23)$$

Since $[4\pi(\Delta P+P_E)+E]$ is the electric displacement for fields above the saturation effect, the dielectric constant for values of the field so high that domain saturation has set in will be

$$\epsilon_s=D/E=\epsilon_0$$
$$+4\pi A/\beta[A^3(P_s/N\mu)^2-(A-1)]. \quad (24)$$

At 0°C, $P_s=740$ e.s.u., $N\mu=3700$ e.s.u., $A=1.014$ and $\beta=4.07$. Hence the saturation dielectric constant for the clamped crystal should have a value of 114. This agrees reasonably well with the measured value[12] of 200 at 20°C, where the saturation dielectric constant should be somewhat higher due to the smaller denominator of Eq. (24).

The theoretical value of the coercive field required to reverse a single domain can also be calculated from Eq. (22). If we plot the curve on a graph, the shape is shown in an exaggerated form in Fig. 8. To determine the coercive voltage required to change the polarization to the opposite sign, we have to raise E (negative) until

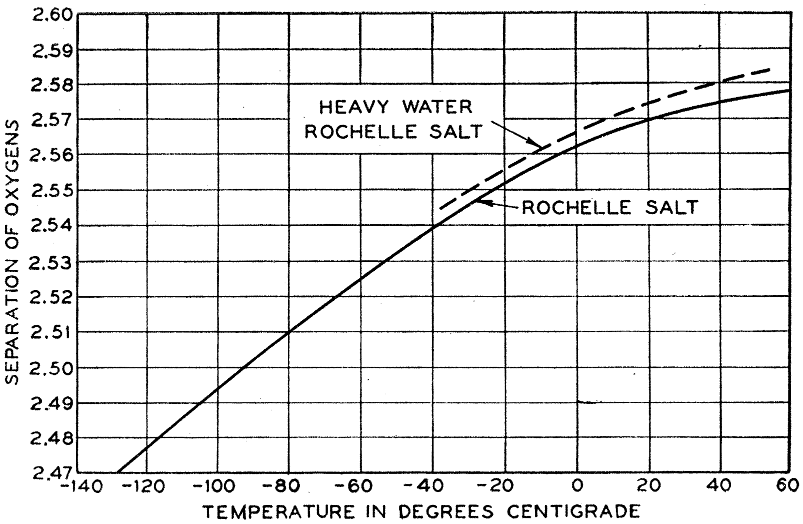

FIG. 7. Calculated separation of oxygens in rochelle salt and heavy water rochelle salt as a function of temperature.

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[12] Reference 1, p. 569.

$-6.7\times10^{-5}\,E$ equals the greatest deviation of the hyperbolic tangent from the straight line going through zero and the solutions $P_d/N\mu=0.20$. By calculation, this occurs when $P_d/N\mu=0.12$ and it requires a coercive field of 16 esu or 4800 volts cm. As with the phenomenological theory, this is about 16 times the experimental value. An explanation of this discrepancy has been given by Cady.[13] The effect is caused by the other domains contributing a field determined by the applied electric field, which cuts down the value of the applied field necessary to reverse the domain.

III. CLAMPED DIELECTRIC CONSTANT AT LOW FIELD STRENGTHS

A solution of Eq. (11) for small applied voltages also accounts quantitatively for the measured values of the clamped dielectric constant at low field strengths over a frequency and temperature range. For simple harmonic motion we let

$$E=E_0e^{j\omega t};\quad P_d=P_s+P_0e^{j\omega t}$$

where P_s is the spontaneous dipole polarization. Also since the time-variable field and polarization are small compared to the spontaneous effect, we can write

$$\sinh A\left[\frac{E_0e^{j\omega t}}{\beta N\mu}+\frac{(P_s+P_0e^{j\omega t})}{N\mu}\right]$$
$$=\sinh A\left[\frac{E_0}{\beta N\mu}+\frac{P_0}{N\mu}\right]e^{j\omega t}\cosh\frac{AP_s}{N\mu}$$
$$+\cosh A\left[\frac{E_0}{\beta N\mu}+\frac{P_0}{N\mu}\right]e^{j\omega t}\sinh\frac{AP_s}{N\mu}$$

and since the time variable parts are very small

$$\sinh A\left[\frac{E_0+\beta P_0}{\beta N\mu}\right]e^{j\omega t}\doteq\frac{A[E_0+\beta P_0]e^{j\omega t}}{\beta N\mu};$$

$$\cosh A\left[\frac{E_0+\beta P_0}{\beta N\mu}\right]e^{j\omega t}\doteq 1$$

Then Eq. (11) takes the form

$$\Gamma^{-1}e^{\Delta U/kT}j\omega P_0e^{j\omega t}$$
$$=N\mu\left[\sinh\frac{AP_s}{Nu}+\frac{A(E_0+\beta P_0)}{\beta N\mu}e^{j\omega t}\cosh\frac{AP_s}{N\mu}\right]$$
$$-(P_s+P_0e^{j\omega t})\left[\cosh\frac{AP_s}{N\mu}+\frac{A(E_0+\beta P_0)}{\beta N\mu}\times e^{j\omega t}\sinh\frac{AP_s}{N\mu}\right].\quad(26)$$

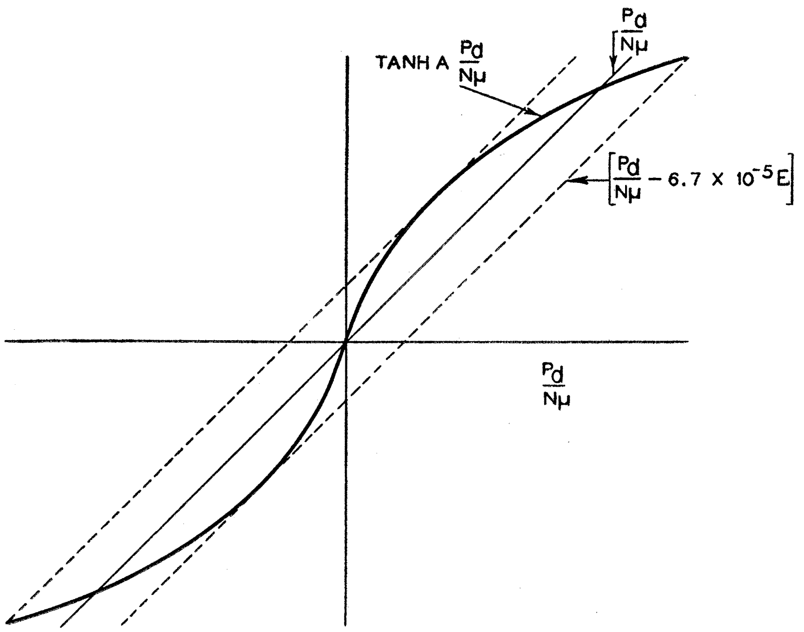

FIG. 8. Value of Eq. (22) plotted as a function of $P_d/N\mu$.

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[13] Reference 1, p. 654.

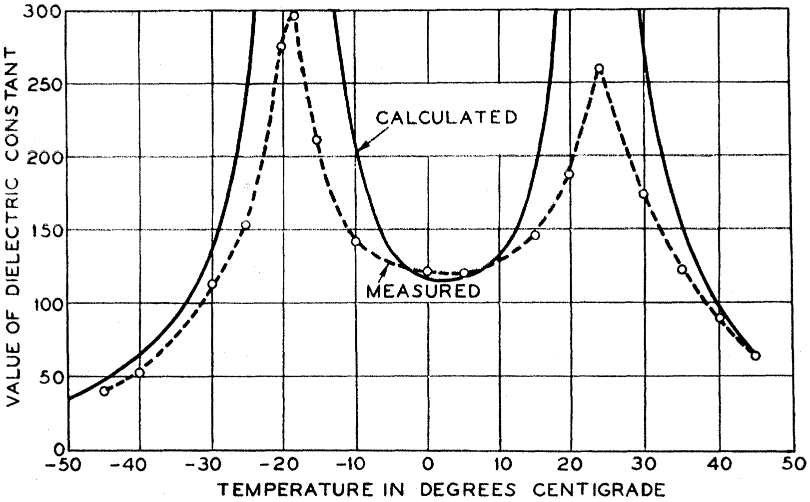

Fig. 9. Measured and calculated values of the clamped dielectric constant for low field strengths plotted as a function of temperature.

Collecting the constant terms we have again the equation for spontaneous polarization

$$\tanh(AP_s/N\mu)=P_s/N\mu, \tag{13}$$

while the time variable polarization can be written in the form

$$P_0=\frac{(A/\beta)[1-(P_s/N\mu)^2]E_0}{1-A[1-(P_s/N\mu)^2]+j\omega e^{\Delta U/kT}/\Gamma\cosh(AP_s/N\mu)}. \tag{27}$$

The electric displacement D is equal to

$$D=4\pi P_0+4\pi P_E+E=\epsilon E \tag{28}$$

where P_E is the electronic and atomic polarization and ϵ the dielectric constant. Hence the dielectric constant of the clamped crystal for small applied fields takes the form

$$\epsilon=\epsilon_0+\frac{(4\pi A/\beta)[1-(P_s/N\mu)^2]}{1-A[1-(P_s/N\mu)^2]+j\omega e^{\Delta U/kT}/\Gamma\cosh(AP_s/N\mu)}. \tag{29}$$

where ϵ_0 is the dielectric constant for electrons and atoms alone which has been assumed to be $\epsilon_0=6.0$.

The measured value of the spontaneous polarization is given by Fig. 5. From this and the calculated value of A given by Fig. 6, the calculated value of the clamped dielectric constant of rochelle salt is found as shown by Fig. 9. This quantity was measured at frequencies of about 160 kilocycles by measuring[14] the longitudinally clamped dielectric constant (i.e., the dielectric constant when longitudinal motion is suppressed), and correcting for the remaining motion. This was measured from -10°C to $+50$°C and is shown plotted by the solid line of Fig. 10. In order to eliminate any corrections, and to extend the temperature range, the dielectric constant of the clamped crystal has been measured by measuring the dielectric constant of an X-cut rochelle salt crystal at 20 megacycles. The dimensions of the crystal were 1.75 cm by 1.75 cm in cross section and 0.759 cm thick (thickness along X axis). This is so high a frequency that the added capacity due to any piezoelectric resonances is negligible and the measured capacity is directly the clamped dielectric constant. The measured values of the dielectric constant and the Q of the crystal are shown plotted by the dashed line. The measured values agree quite well with those obtained previously. The points of highest capacity come at -18°C and $+24$°C which, as mentioned in the introduction, show conclusively that the anomaly must reside in the clamped dielectric constant. The measured values are somewhat lower than the calculated values obtained from Eq. (29) using the values of A from Fig. 6, the spontaneous polarization from Fig. 5, the value of $N\mu=3850$ e.s.u. at 24°, 3550 at -18°, and a proportional value for any other temperature, a value of $\beta=4.07$ and a value of $\epsilon_0=6$.

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[14] W. P. Mason, Phys. Rev. **58**, 747 (1940).

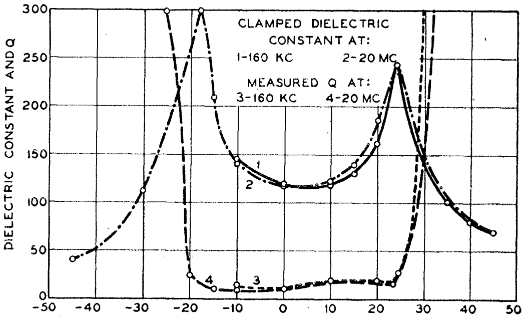

FIG. 10. Measured value of clamped dielectric constant and associated Q for low field strengths plotted as a function of temperature.

Equation (29) also accounts for some recent measurements of W. A. Yager on the dielectric constant of rochelle salt at a frequency of 2.5×10^{10} cycles. Yager finds that from $-40°\text{C}$ to $+26°\text{C}$ the dielectric constant and the Q of rochelle salt are practically independent of temperature and have the values

$$\epsilon=8;\quad Q=0.25. \tag{30}$$

These measurements were made by a wave-guide technique. They indicate that the frequency is so high that the hydrogen bond dipoles cannot follow the field, and contribute little to the dielectric constant.

The impedance to be expected theoretically can be calculated from Eq. (29). This results in

$$\frac{1}{Z}=\frac{1}{Z_d}+\frac{1}{Z_0}=j\omega\frac{\epsilon\times1.11\times10^{-12}}{4\pi}=j\omega\times1.11\times10^{-12}$$
$$\times\left[\frac{(A/\beta)[1-(P_s/N\mu)^2]}{1-A[1-(P_s/N\mu)^2]+j\omega e^{\Delta U/kT}/\Gamma\cosh(AP_s/N\mu)}+\frac{\epsilon_0}{4\pi}\right].$$

This equation is the impedance of two parallel arms, one arm Z_d representing the impedance of the dipole term and the other, the impedance Z_0, is the impedance of a condenser with a dielectric constant ϵ_0 due to other types of polarization. The impedance of the dipole arm per cubic cm is

$$Z_d=9\times10^{11}\left[\frac{\beta}{A(1-(P_s/N\mu)^2)}\right]\left\{\left[\frac{\Gamma^{-1}e^{\Delta U/kT}}{\cosh(AP_s/N\mu)}\right]\right.$$
$$\left.-\frac{j}{\omega}[1-A(1-(P_s/N\mu)^2)]\right\}. \tag{31}$$

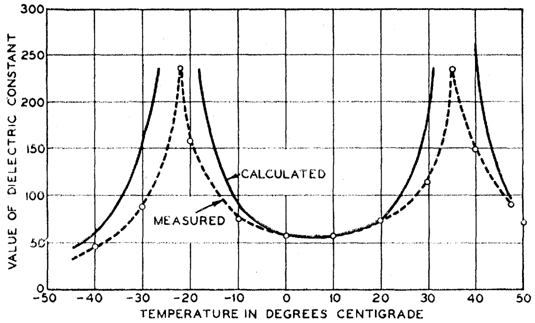

FIG. 11. Measured and calculated values of the clamped dielectric constant of heavy water rochelle salt.

The impedance of the other arm with the dielectric constant ϵ_0 is

$$Z_0=-\frac{j}{\omega C_0}=-\frac{j9\times10^{11}\times4\pi}{\omega\epsilon_0}. \tag{32}$$

In evaluating this equation we now assume the value of Γ given by Eyring's reaction rate theory, namely $\Gamma=(kT/h)$. At a frequency of 2.5×10^{10} cycles and at a temperature of 0°C, the impedance of the dipole arm, assuming $\beta=4.07$;

$$A=1.014,\quad (P_s/N\mu)=0.20,\quad h=6.55\times10^{-27},$$
$$k=1.37\times10^{-16},\quad T=273,\quad \Delta U=1100$$

calories per mole, is

$$Z_0=3.2-j0.63 \tag{33}$$

and hence the resistance component is larger than the reactance component. The indicated relaxation frequency is about 5×10^9 cycles at 0°C. Furthermore we see that the value of the resistance will not change much with temperature since $(\Delta U/kT)$ decreases as we decrease the temperature and this offsets the increase due to $1/kT$. Hence the measured capacitance shunted by the resistance will be relatively independent of the temperature over the region $-40°\text{C}$ to $+20°\text{C}$. The measured results of Yager given by Eq. (30) indicate that the impedance per cm³ at 2.5×10^{10} cycles, should be a reactance $-j9.0$ ohms in parallel with a resistance $\frac{1}{4}$ this value, or 2.25 ohms. Neglecting the reactance $-j0.63$ in Eq. (33) the resistance value is within a factor of 2 of the measured value and indicates that the best separation of oxygens is about 2.57A. The indicated dielectric constant of 8 is somewhat larger than the value 6 assumed, but since the value 8 is a preliminary result it agrees reasonably well with the value 6.0 assumed. Hence the present theory accounts approximately for the clamped dielectric constant and the spontaneous polarization for all temperatures and frequency ranges. It involves only molecular constants that can in principle be determined by x-ray measurements, rather than the phenomenological constants.

The present theory does not account for the finite value of the clamped dielectric constant at the Curie points nor the hysteresis resistance at small amplitudes both inside and outside of the Curie temperatures, which is evidenced by the nearly constant values of Q, *versus* frequency, shown by the curves of Fig. 10. It is thought that these effects may be due to the fact that the hydrogen bond 1 to 10 may be part of a chain of three hydrogen bonds. When a displacement occurs in the 1 to 10 bond it may generate coupled displacements for the connecting bonds which react back on the 1 to 10 bond. This would cause a hysteresis loop since it would require a reverse force to undo the effect of the connecting link displacement and the loss of energy to the connecting bonds may also be the cause of the finite dielectric constant at the Curie temperatures.

IV. APPLICATION OF THEORY TO HEAVY WATER ROCHELLE SALT

When the hydrogens in the water molecules and the hydroxyl molecules are replaced by heavy hydrogens, a very considerable change occurs in the properties of the rochelle salt crystal. As shown[15] by Fig. 5, the lower Curie point is lowered to $-22°$C, the upper one raised to 35°C and a considerably larger spontaneous polarization occurs. The properties of heavy water rochelle salt provide a good test of the present theory. They are accounted for if we assume that the separation of the oxygens is increased in the heavy water rochelle salt over ordinary rochelle salt.

From the ratio of the spontaneous polarization 1120 e.s.u. to the value of $N\mu$ which is still about 3700 e.s.u., and the curve of Fig. 3, one can see that the replacement of hydrogen by heavy hydrogen has resulted in the factor

$$A = e^2\delta^2 N\beta \cos^2 25°/4kT(1-\beta\gamma) = 1.033,$$

at 6°C for which the highest value of A occurs. To account for this value and $A=1$ at $-22°$C and $+35°$C, the oxygen separation *versus* temperature occurs as shown by the dashed line of Fig. 7. In general this separation parallels that for the ordinary rochelle salt, but at the higher temperature shows less bending off than does that for ordinary rochelle salt. This is probably accounted for by the double weight of the heavy hydrogen nucleus. Using these values of separations, the values of A for heavy water rochelle salt are shown plotted by the dot-dash line of Fig. 6.

From the value of A given by Fig. 7 and the measured value of the spontaneous polarization shown by Fig. 5, the calculated clamped dielectric constant is shown plotted by Fig. 11. The measured values can be obtained from previous measurements[16] of the free dielectric constant and the piezo-electric constant, and are shown plotted by the dotted line of Fig. 11. This agrees well with the calculated value.

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[15] J. Hablutzel, Helv. Phys. Acta. **12**, 489 (1939).

[16] A. N. Holden and W. P. Mason, Phys. Rev. **57**, 54 (1940). J. Hablutzel, Helv. Phys. Acta. **12**, 489 (1939).