PHYSICAL REVIEW VOLUME 168, NUMBER 2 10 APRIL 1968

Dielectric Relaxation of Rochelle Salt*

F. SANDY† AND R. V. JONES
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

(Received 16 August 1967)

The complex dielectric constant of Rochelle salt has been measured at frequencies from 2.5 to 13 GHz, and at 155 MHz. The measurements were made in a temperature range from −50 to 45°C which includes the ferroelectric region and significant parts of both paraelectric regions. Measurements were made both with and without dc biases. The dielectric constant is found to undergo a relaxation of a strictly Debye character. Over the entire temperature range, the relaxation time is found to be proportional to $T^{1.25}$ times the difference between the low-frequency, clamped, differential dielectric constant and its limiting high-frequency value. This result is shown to be consistent with a model of the high-frequency dielectric behavior based on the Kubo susceptibility formalism. Following Mitsui, it is assumed that the ferroelectric properties of Rochelle salt arise from the rotation of hydroxyl groups within the tartrate molecules. The basic relaxation process probably involves phonon-induced transitions between the lowest states of these hydroxyl ions. However, the cooperative dipolar interaction between ions reduces the over-all relaxation rate of the coupled system. An approximate model Hamiltonian of the coupled hydroxyl system is constructed in terms of the Pauli matrices and is used to calculate an explicit expression for the relaxation rate.

I. INTRODUCTION

IT was the investigations of the unusual properties of Rochelle or Seignette salt that first led to the evolution of the notion of *ferro-electricity*.[1–3] Since the early work on this substance numerous materials, of course, have been found to exhibit similar ferroelectric properties. However, Rochelle salt (sodium potassium tartrate tetrahydrate, $NaKC_4H_4O_6 \cdot 4H_2O$) remains essentially unique in that its ferroelectric region lies in a narrow temperature range between −18 and +24°C. Above and below this temperature range the nonpolar regions appear to be crystallographically identical. Mitsui,[4] drawing on the earlier work of Mueller,[5] Mason,[6] and Devonshire,[7] has developed a model which accounts rather well for the peculiar static ferroelectric characteristics of this material.

In this paper, we report a series of measurements of the complex dielectric constant of Rochelle salt in the frequency range from 2.5 to 13 GHz. Within this range, the ferroelectric properties exhibit a distinct Debye-type relaxation. These measurements were made in the ferroelectric region and in significant parts of both nonpolar regions. In order to make contact with the theoretical analysis, measurements were also made at a single *low* frequency, viz., 155 MHz. We have found that this frequency is low compared to the dielectric relaxation frequency of Rochelle salt, but high compared to the piezoelectric resonance frequencies of our samples. In this way, we are measuring consistently dielectric constants at constant strain (clamped dielectric constant) rather than at constant stress (free dielectric constant). It is, of course, the clamped dielectric constant which is directly susceptible to theoretical analysis. We will show that all of our experimental results are consistent with a rather elementary extension of Mitsui's model[4] of static behavior. However, our results differ in several important respects from those obtained both experimentally and theoretically for other ferroelectrics. For prospective it is useful to review, briefly, some of the previous work on the frequency dependence of ferroelectric dielectric constants.

A rather sophisticated model of "displacive" ferroelectricity has been developed by Cochran[8] and others[3] in terms of instabilities in the lattice vibrations. Cochran has shown that the spontaneous ferroelectric distortion may result from a transverse optical phonon of zero (or near zero) wave vector becoming unstable at the Curie temperature. In the paraelectric region, the square of the frequency of this mode ω_F^2 decreases linearly with temperature, becoming zero at the Curie temperature, at which point the harmonic motion of this mode becomes unstable and a phase change is possible. According to this view, the frequency-dependent dielectric constant should have the form

$$\epsilon(\omega) \propto (\omega_F^2 - \omega^2)^{-1}. \qquad (1)$$

Rigorously, a damping term is also necessary in the above equation and the nature of the damping processes has been discussed by Silverman.[9] When $\omega = 0$, Eq. (1) and a linear temperature dependence of ω_F^2 yield the familiar Curie-Weiss law. Experimentally, the di-

---

* Research supported by the Electronics Research Directorate of the U.S. Air Force Cambridge Research Laboratories, Office of Aerospace Research under Contract No. AF 19(628)-3874.

† Present address: Raytheon Research Division, Waltham, Mass.

[1] J. Valasek, Phys. Rev. **17**, 475 (1921); **19**, 478 (1922); **20**, 639 (1922); **24**, 560 (1924); Science **65**, 235 (1927).

[2] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Co., New York, 1964).

[3] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

[4] T. Mitsui, Phys. Rev. **111**, 1259 (1958).

[5] H. Mueller, Phys. Rev. **47**, 175 (1935); **57**, 829 (1940); **58**, 565 (1940); **58**, 805 (1940); Ann. N.Y. Acad. Sci. **40**, 321 (1940).

[6] W. P. Mason, Phys. Rev. **72**, 1 (1957); *Piezoelectric Crystals and Their Applications to Ultrasonics* (D. Van Nostrand Inc., Princeton, N.J., 1950).

[7] A. F. Devonshire, Phil. Mag. **2**, 1027 (1957).

[8] W. Cochran, Advan. Phys. **9**, 387 (1960); **10**, 401 (1961).

[9] B. D. Silverman, Phys. Rev. **125**, 1921 (1962).

electric constant in displacive ferroelectrics such as $BaTiO_3$ has been found to go through a resonance in the far infrared.[10,11] As predicted by theory, the resonance frequency varies with temperature as $(T-T_c)^{1/2}$ and, hence, as $(\epsilon_0)^{-1/2}$ where ϵ_0 is the low-frequency, clamped, dielectric constant.

In contrast, the dielectric dispersions in several of the so called "order-disorder" ferroelectrics have been found to be of a relaxation character. Hill and Ichiki[12] have observed a broad relaxation, at microwave frequencies, in the dielectric constant of deuterated potassium dihydrogen phosphate (KDP), triglycine sulfate (TGS), and deuterated TGS with a relaxation time proportional to ϵ_0. The shape of this relaxation was approximated by a Gaussian distribution of Debye relaxation functions of the form

$$\epsilon(\omega) \propto \int_0^\infty \exp(-\alpha^2\tau^2)(1+i\omega\tau)^{-1}d\tau. \qquad (2)$$

The dispersion in Rochelle salt was first observed by Akao and Sasaki.[13] They also reported a broad relaxation in the microwave region whose relaxation time varied as ϵ_0. However, subsequent measurements by Jackle,[14] at 9.39 GHz, and by Horioka and Abe[15] at 9.30 GHz, near the upper Curie temperature and by Baumler, Blum, and Deyda[16] at 9.61 GHz over the temperature range from −30 to 40°C show large (up to a factor of 3) errors in Akao and Sasaki's results. In large part, these errors arose from the small air gap between their unplated samples and the walls of their wave-guide sample holder. Later measurements by Petrov[17] on Rochelle salt also appear to suffer from a residual air gap. This gap acts as a thin series capacitor with an extremely low relative dielectric constant and tends to mask the capacitance of the ferroelectric material.

The measurements reported here cover a much larger frequency range than those of Jackle[14] and Baumler *et al.*[16] However, the agreement between our results and theirs is quite good in the region of overlap. The experimental procedures used in this work are outlined in Sec. II. The experimental results are discussed in Sec. III where it is shown that the temperature dependence of the relaxation time arises mainly from a proportionality to ϵ_0, but has an additional explicit temperature dependence of the form T^N where N is approximately 5/4. However, the shape of the relaxation is very close to a pure Debye relaxation[18] rather than the broad relaxation observed in other order-disorder ferroelectrics. In Sec. IV an extension of Mitsui's model is presented which makes use of the Kubo formulism for complex susceptibilities.[19]

II. EXPERIMENTAL PROCEDURE

Three different experimental techniques were used in this investigation in order to cover the entire frequency range. At the high end of the frequency range, 9.5 to 13 GHz, the reflection coefficient of a wave guide completely filled with a silvered block of Rochelle salt was measured with a slotted line. The sample was long enough to completely attenuate any reflections from its rear face. Even at these high frequencies the dielectric constant of Rochelle salt is quite large and a filled guide has a reflection coefficient very close to minus one. While the large resultant voltage standing-wave ratio (VSWR) was not hard to measure accurately, the very small difference in phase between the reflected wave from the sample and a perfect short (typically 0.005 wavelengths) was difficult to measure. In order to increase the phase shift, the sample holder was partially matched to the slotted line by means of a quarter wavelength section of wave guide filled with Rexolite having a dielectric constant of 2.55. The reflection coefficient from the front of this transformer was then close to that of an open circuit but differed from it in phase by an amount adequate for measurements to be made at frequencies up to the low end of K_u band. Above that point spurious reflections from sample irregularities became relatively larger and precluded accurate measurements.

The reference phase was established in these measurements by measuring the position of a null in the slotted line when a short was placed at the far end of the empty sample holder. To this null position was added the length of the sample plus transformer to obtain the position of a null due to a short at the front face of the transformer. Minor corrections in the null position were then made for the difference in guide wavelength between the sample holder and slotted line, the change in length of the sample holder with temperature and the change in guide wavelength of the sample holder due to thermal expansion of its cross section. The temperature of the sample was controlled by immersing the holder in a Dewar containing water (at or above room temperature) or alcohol (below room temperature).

At frequencies from 2.5 to 9.5 GHz the dielectric constant was determined by measuring the capacitance of a small disk of Rochelle salt approximately 70 mils in diameter and 39 mils thick. The disk was silvered on both faces and placed between the center conductor of a

---

[10] A. S. Barker and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

[11] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).

[12] R. M. Hill and S. K. Ichiki, Phys. Rev. **128**, 1140 (1962); **130**, 150 (1963); **132**, 1603 (1963).

[13] H. Akao and T. Sasaki, J. Chem. Phys. **23**, 2210 (1955).

[14] W. Jackle, Z. Angew. Phys. **12**, 148 (1960).

[15] M. Horioka and R. Abe, J. Appl. Phys. Japan **5**, 1114 (1966).

[16] P. Baumler, W. Blum, and H. Deyda, Z. Physik **180**, 96 (1964).

[17] V. M. Petrov, Kristallografiya **7**, 403 (1962) [English transl.: Soviet Phys.—Cryst. **7**, 319 (1962)].

[18] P. Debye, *Polar Molecules* (Dover Publications, Inc., New York, 1929).

[19] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

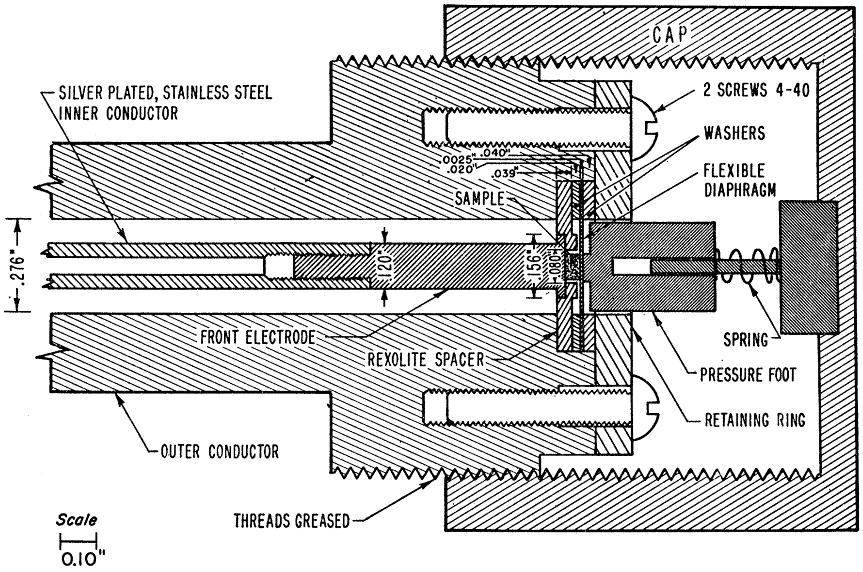

FIG. 1. Coaxial sample holder for dielectric measurements.

rigid coaxial line and a flexible diaphragm terminating the outer conductor. A diagram of the end of the coaxial sample holder is shown in Fig. 1. The impedance of the sample plus holder is measured with a slotted line as shown in the block diagram, Fig. 2. This technique is similar to that used by Jaynes and Varenhorst,[20] Diamond,[21] and Hill and Ichiki[12] at lower microwave frequencies. However, at the high end of the frequency range involved, it is no longer valid to treat the system as a uniform transmission line terminated with the sample impedance plus a fixed capacitance and inductance representing the fringing fields of the sample holder as is done at lower frequencies. Not only does this lumped circuit for the fringing fields break down, but the attenuation of the sample holder and the reflections from the connector between the slotted line and the sample holder become noticeable. The transformation of the impedance of the sample through the holder and slotted line (or any microwave network for that matter) can, however, always be simulated by the transformation through any of numerous three component circuits. These components, of course, have an unknown frequency dependence and hence must be measured at each frequency used. The calibration procedure, which employed a set of disks of known dielectric constant having the same shape as the Rochelle salt samples, is described in detail in Ref. 22. That report also describes the corrections in calculating the impedance of the small Rochelle salt capacitors. These corrections are necessitated by the fact that the radius of the disks while small is not negligible compared to a wavelength in the material at the frequencies employed.

Provisions were made for inserting a dc bias on the center conductor of the sample holder. It was found necessary, however, to switch the polarity of this bias several times per minute to avoid the build up of a dipole layer at the sample surface with a large part of the dc bias across it. This layer, it is assumed, arises from the difference between the bulk and surface resistivities of the sample.

The low-frequency, clamped, dielectric constant was measured by means of a General Radio uhf bridge at 155 MHz using the same coaxial sample holder and ferroelectric samples. Since the samples had a very high impedance at this low frequency and the bridge was capable of measuring from a smaller upper limit down to zero, an odd number of quarter wavelengths of line was placed between the sample and the bridge. The length of the line was then adjusted so that the bridge read zero for the empty sample holder. The deviations in the length of the line from $\frac{3}{4}$ wavelengths then just balanced the capacitance of the fringing fields at the end of the sample holder.

III. EXPERIMENTAL RESULTS

Microwave Measurements

The microwave measurements of the real part of the dielectric constant of our best samples of Rochelle salt are shown in Fig. 3. The various curves were taken at fixed frequencies indicated by distinct points. Results among good samples agreed within about 10%. This sample-to-sample scatter is about twice as large as the total instrumental error.

The most interesting qualitative feature of these results is that at all frequencies above 5.10 GHz, and

---

[20] E. T. Jaynes and V. Varenhorst, Stanford University, Microwave Laboratory Rept. 287, 1956 (unpublished).

[21] H. Diamond, University of Michigan, Willow Run Laboratory Report of Project Michigan 2900-121-T, 1960 (unpublished).

[22] F. Sandy, Air Force Cambridge Research Laboratories Report 65-250, 1965 (unpublished).

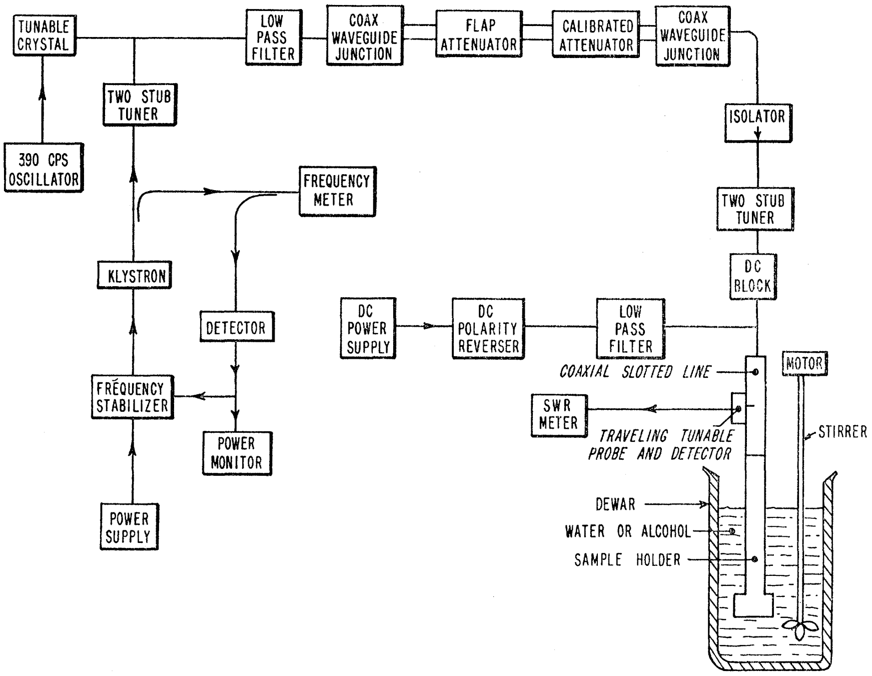

FIG. 2. Block diagram of coaxial system used for measurements in the range 2.5 to 9.5 GHz.

possibly even at 3.90 GHz, the real part of the dielectric constant has minima at the Curie temperatures, instead of maxima. The reason for these minima may be understood quite simply. We might assume that in accordance with results of previous workers, the relaxation frequency varies inversely with the low-frequency, clamped, dielectric constant. It is intuitively reasonable that a better approximation would use the difference between the low-frequency dielectric constant and the high-frequency limit that the dielectric constant is approaching, rather than the low-frequency value alone. We may thus write

$$\epsilon'-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)f(\omega\tau),$$
$$\tau=\tau_0(\epsilon_0-\epsilon_\infty), \tag{3}$$

where ϵ' is the real part of the dielectric constant, ϵ_0 and ϵ_∞ are, respectively, its low- and high-frequency values, $f(\omega\tau)$ is an, as yet, unknown relaxation function, and τ_0 is a constant of proportionality.

We now wish to find how ϵ' varies with temperature at high frequencies. Differentiating Eq. 3 and assuming that $\partial\tau_0/\partial T$ is zero or negligible, we may write

$$\frac{\partial\epsilon'}{\partial T}=\frac{\partial\epsilon_0}{\partial T}f(\omega\tau)\left[1+\frac{\partial\ln f(\omega\tau)}{\partial\ln(\omega\tau)}\right]. \tag{4}$$

Since $\epsilon'-\epsilon_\infty$ is positive, $f(\omega\tau)$ must be positive. Thus, $\partial\epsilon'/\partial T$ has the same sign as $\partial\epsilon_0/\partial T$, providing $\partial\ln f(\omega\tau)/\partial\ln(\omega\tau)>-1$. If it is less than -1, ϵ' has the opposite slope to that of ϵ_0. This is just what is observed near the Curie temperatures at high frequencies. The requirement that the logarithmic derivative be less than -1 above some frequency implies that $f(\omega\tau)$ falls off faster than ω^{-1} at high frequencies. Now the relaxation described by Hill and Ichiki as shown in Eq. (2) has a limiting fall-off of ω^{-1} and, hence, the logarithmic slope is always greater than -1. For this reason one does not find minima at the Curie temperatures in KDP or TGS. However, a pure Debye relaxation of the form $(1+\omega^2\tau^2)^{-1}$ has a limiting fall-off of ω^{-2} and the logarithmic derivative is less than -1 for all $\omega>1/\tau$. As will be seen later in this section, the relaxation in Rochelle salt is in fact of the Debye type. It will also be seen that the proportionality constant τ_0 is not entirely temperature-independent. However, its temperature dependence is so small compared to that of ϵ_0 that it may be ignored in the above discussion.

The data in Fig. 3 may be essentially characterized in the following way. The dielectric constant drops with frequency at all temperatures. However, since $\epsilon_0-\epsilon_\infty$ is greatest at the Curie temperatures, the relaxation frequency is lowest there. The dielectric constant thus starts to drop first at the Curie temperatures, and if it drops at a fast enough rate it can become less than the dielectric constant at neighboring temperatures.

Since the relaxation frequency is proportional to $(\epsilon_0-\epsilon_\infty)^{-1}$ and the criterion that the slope $\partial\epsilon'/\partial T$ have the opposite sign to $\partial\epsilon_0/\partial T$ is that the measurement frequency be greater than the relaxation frequency, one would expect that the temperature range in which this inversion takes place would increase with frequency. This is in fact the case, as can be seen in Fig. 3. The reason that the existence of a minimum at the Curie temperatures at 3.90 GHz is ambiguous is that the

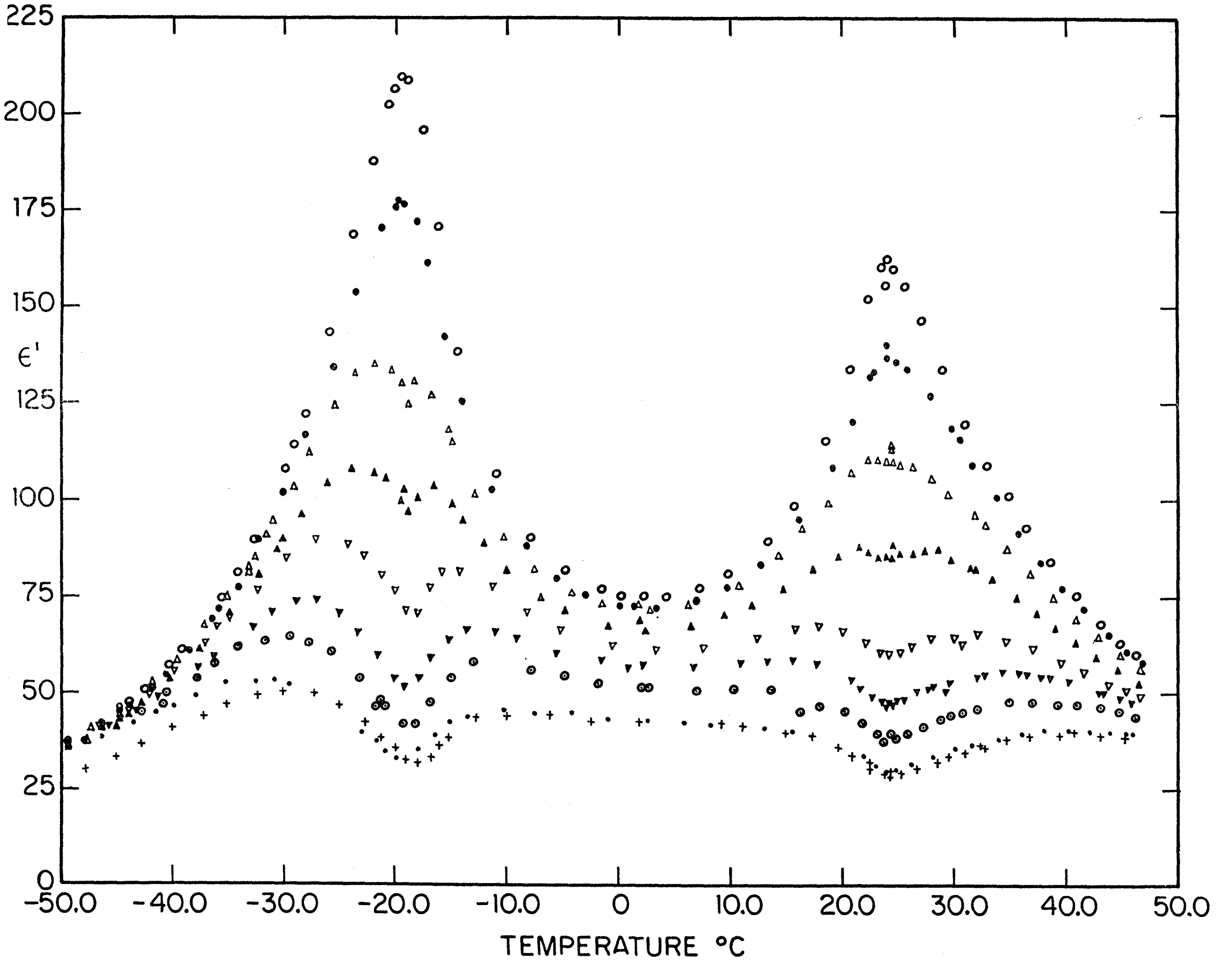

FIG. 3. Temperature dependence of real part of the dielectric constant of Rochelle salt measured at various fixed frequencies (in GHz): 2.5 ○; 3.0 ●; 3.9 △; 5.1 ▲; 7.05 ▽; 8.25 ▼; 9.45 ⊙; 11.96 +; 12.95 •.

temperature range in which the inversion takes place is very small, even though 3.90 GHz is slightly greater than the relaxation frequency at the Curie temperatures. Not only is the range of the inversion small, but the magnitude of the slope $\partial\epsilon'/\partial T$ is small and the curve appears flat, rather than having minima at the Curie temperatures.

The same argument can be applied to the imaginary part of the dielectric constant by replacing $\epsilon'-\epsilon_\infty$ with ϵ'' in Eq. (3). However, the imaginary part of a Debye relaxation goes as $f(\omega\tau)=\omega\tau/(1+\omega^2\tau^2)$. The limiting fall-off of this expression is ω^{-1} and the logarithmic slope never is less than -1. Thus, in agreement with the experimental observation, the imaginary part of the dielectric constant would not be expected to have minima at the Curie points—see Fig. 4.

Low-Frequency Measurements

Before we can go on to determine the form of the relaxation function, it is necessary to discuss the appropriate values to use for the temperature dependence of ϵ_0. Values of the low-frequency, clamped, dielectric constant have been reported by Mueller,[5] Mason[6], and Akao and Sasaki.[13] Their results are quite inconsistent as can be seen in Fig. 5. Measurements were, therefore, made at 155 Mc/sec by the method described in Sec. II. These are also included in Fig. 5.

It is interesting to note the results reported here agree within 10% with Mason's results in the nonpolar regions, but are only 60% of Mason's values in the middle of the ferroelectric range. The reason for this discrepancy is believed to be the following. Mason's measurements were made at 20 Mc/sec which is a high enough frequency to insure inertial clamping. However, in the ferroelectric region the dielectric constant has two distinct components. The first comes from domain wall motion, while the second arises from the intrinsic $\partial P/\partial E$ within each domain. Apparently, the domain wall resonance occurs somewhere between 20 Mc/sec and 155 Mc/sec, so that Mason's measurements include

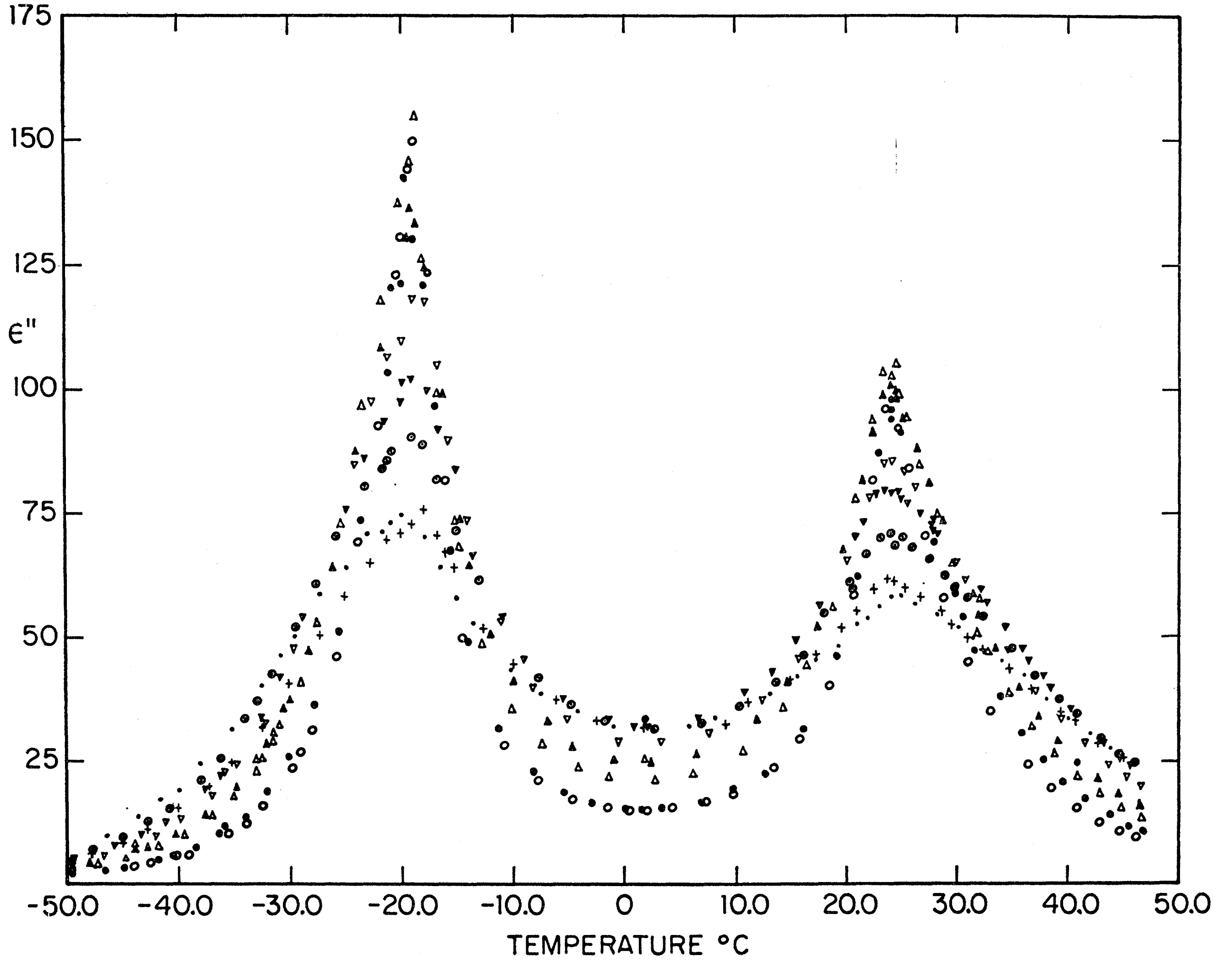

FIG. 4. Imaginary part of dielectric constant of Rochelle salt at various frequencies. Frequencies denoted as in Fig. 3.

the domain wall motion and the results reported here do not. It is only the intrinsic value that we are interested in here. If the values of the dielectric constant measured at microwave frequencies in the middle of the ferroelectric range are extrapolated to zero frequency, they yield a value between 5% and 10% below that measured at 155 Mc/sec. While this may only be experimental error, it is more likely that it indicates that a small contribution from domain wall motion still exists at 155 Mc/sec. In subsequent calculations the measured values have been reduced 5% in accord with this assumption.

Analysis of Data

Using the low-frequency values of the dielectric constant given in Fig. 5 and the measured microwave values, we may plot the frequency dependence of ϵ' and ϵ'' with the temperature as a supressed parameter. For convenience we actually use $(\epsilon'-\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)$ and $\epsilon''/(\epsilon_0-\epsilon_\infty)$ as normalized ordinates. We also use $\nu(\epsilon_0-\epsilon_\infty)$ as a normalized abscissa. If our conjecture that the relaxation time is proportional to $(\epsilon_0-\epsilon_\infty)$, then for all temperatures the normalized quantities should lie on a single curve.

Two such plots with temperature as an implicit variable are given in Figs. 6 and 7. These graphs were plotted by an X-Y plotter driven by an IBM 7094 computer used for the data reduction. The solid line included in these figures is a pure Debye relaxation function. An additional scale factor of 0.0011 has been included in the abscissa so that the Debye relaxation frequency is one when ν is measured in GHz. In these figures, as well as in Figs. 8 and 9, the various points designate data taken in approximately 5°C temperature intervals between −45 and +45°C.

In treating our data we have had to assume a value of ϵ_∞. According to Mitsui's model, at low temperature all of the ferroelectric dipoles are frozen in their lowest states and do not contribute to ϵ_0. Hence, in this region ϵ_∞ which represents the dielectric contributions from all other sources is essentially given by ϵ_0. The low-temperature value of ϵ_0 is measured as 7. If we assume that ϵ_∞ has a temperature dependence comparable to that of ϵ in the two nonferroelectric directions of Rochelle salt, we obtain a value $\epsilon_\infty=9$ in the temperature range of interest.

We see from Figs. 6 and 7 that the relaxation is approximately of the Debye shape, and the relaxation frequency is approximately proportional to $(\epsilon_0-\epsilon_\infty)^{-1}$. However, on looking carefully at these figures, it was noted that most of the points below the curve are from high temperatures, and those above the curve are from low temperatures. We thus see that the relaxation time also has a slight temperature dependence in addition to its dependence on $(\epsilon_0-\epsilon_\infty)$. We shall thus assume that

$$\tau_0 \propto T^N \qquad (5a)$$

or

$$2\pi\tau = (\epsilon_0-\epsilon_\infty)(T/273)^N(0.0011\times10^{-9}), \qquad (5b)$$

where T is the absolute temperature. The T^N dependence is not expected to hold beyond the range of temperatures considered here. In order to find N we replotted the data with the renormalized abscissa $(\epsilon_0-\epsilon_\infty)(T/273)^N(0.0011)$ for various values of N (viz., 1.0, 1.25, 1.50, 2.00) and determined subjectively which one comes closest to yielding a single curve. T itself was normalized to 273°K (0°C), to avoid the necessity of varying the constant scale factor 0.0011 with changes in N. The best fit is obtained with $N=1.25\pm0.25$ and this fit is shown in Figs. 8 and 9.

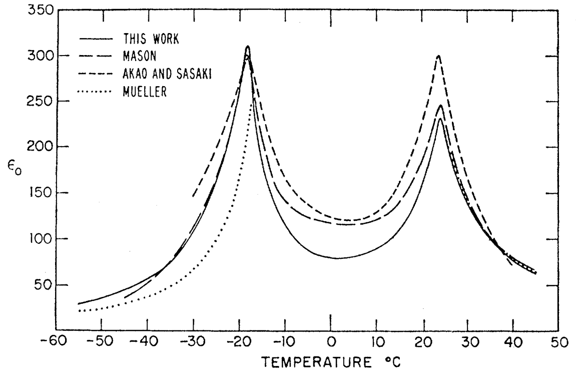

FIG. 5. A comparison of a number of experimentally measured temperature variations in the low-frequency, clampled, dielectric constant ϵ_0. See text for references.

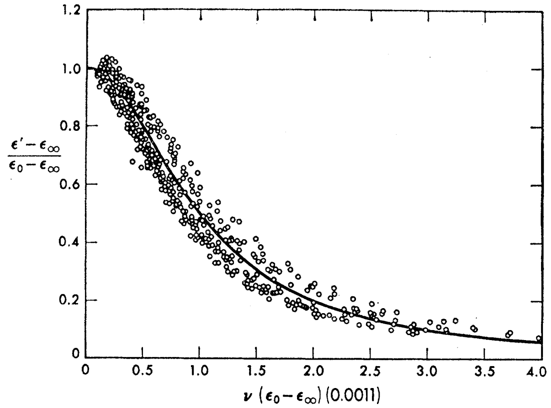

FIG. 6. Real part of normalized dielectric constant of Rochelle salt versus normalized frequency. Temperature is taken as an implicit variable in these plots. Solid curve is a Debye relaxation function.

It may be noticed that while the plots for the real and imaginary parts of the dielectric constant are both improved by this modification of τ, the residual scatter is greatest in the imaginary part. This is easily explainable, if one assumes that the major part of sample-to-sample and run-to-run fluctuations is a result of variations in ϵ_0. These variations are caused by sample strains and imperfections. We assume further that these imperfections affect the relaxation time primarily through its dependence on ϵ_0. Since $\epsilon_0\gg\epsilon_\infty$, the dielectric constant is approximately

$$\epsilon'=\frac{\epsilon_0}{1+\nu^2\{0.0011(T/273)^N\epsilon_0\}^2} \qquad (6a)$$

$$\epsilon''=\frac{\epsilon_0\nu\{0.0011(T/273)^N\epsilon_0\}}{1+\nu^2\{0.0011(T/273)^N\epsilon_0\}^2}. \qquad (6b)$$

We now look to see how a small error in ϵ_0 affects ϵ' and ϵ''. When $\nu\{0.0011(T/273)^N\epsilon_0\}=1.0$, that is, at frequencies near the relaxation frequency, ϵ' is nearly independent of ϵ_0 while ϵ'' depends linearly on ϵ_0. Thus, as we have seen in Figs. 8 and 9, near the normalized frequency of one, ϵ' shows very little scatter and ϵ'' shows considerable scatter. At low frequencies, ϵ' varies linearly with ϵ_0, and experimentally it is seen the scatter gets large. ϵ'' in this region varies as ϵ_0^2, so that its relative scatter also increases. However, since ϵ'' itself gets small in this region, the absolute scatter decreases. ϵ' is also dependent on ϵ_0 at high frequencies,

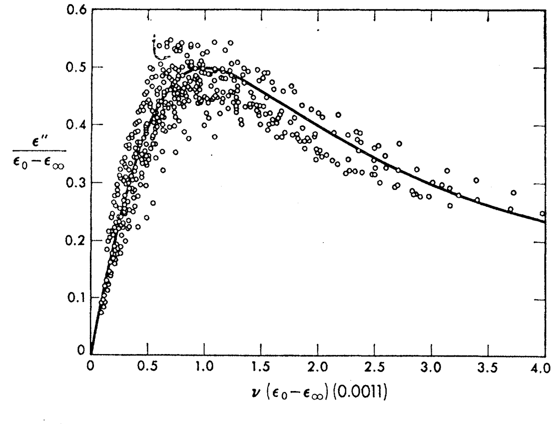

FIG. 7. Imaginary part of normalized dielectric constant of Rochelle salt versus normalized frequency. Solid curve is a Debye relaxation function.

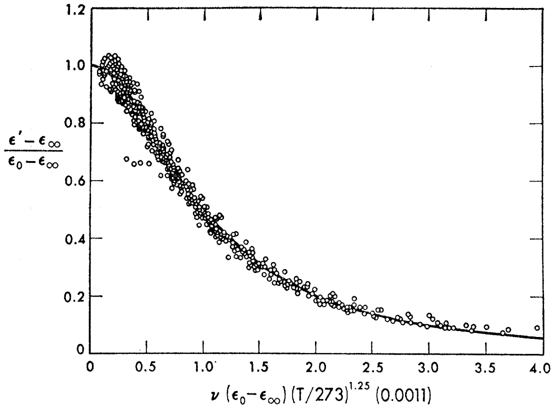

FIG. 8. Real part of normalized dielectric constant of Rochelle salt versus normalized frequency times $(T/273)^{1.25}$. Solid curve is a Debye relaxation function.

but since its magnitude decreases, the absolute scatter is small. On the other hand, ϵ'' becomes independent of ϵ_0 for high frequencies, and the scatter decreases considerably at the high-frequency end even before ϵ'' becomes small itself.

Results in the Ferroelectric Range

One of the original questions posed at the start of this work was whether there were any differences in the high-frequency dielectric behavior between the two nonpolar and the ferroelectric regions. We have already seen that there is no major difference between these regions although there is the apparently continuous dependence of τ_0 on T. However, a careful look at Fig. 8 in the vicinity of the normalized frequency of one, shows that the points in the middle of the ferroelectric range are primarily under the solid curve. In fact, we can say that the relaxation time in the center of the ferroelectric region is given by Eq. (5) times a factor of 1.1 ± 0.1. However, this effect, like the dependence of τ_0 on T, is quite small, and we see that the high-frequency dielectric behavior is qualitatively the same in all three regions.

Effect of a dc Bias

The results that were obtained from measurements with a dc bias applied are summarized below. At 155 MHz and at low-microwave frequencies, the real part of the dielectric constant drops with bias at all temperatures, although in both nonpolar regions the magnitude of the change is small far from the Curie temperatures. As the bias is increased, the temperature of the maximum in ϵ' moves into the nonpolar region. At frequencies sufficiently high to produce minima in the real part of the dielectric constant at the Curie temperatures, a rather interesting effect occurs. At temperatures between the maxima in ϵ' near each Curie temperature, ϵ' first rises with bias and then drops. At all other temperatures, it merely drops with bias as it does at low frequencies. As the bias is increased, each pair of maxima tends to coalesce and the minimum between them moves toward the nonpolar region.

The imaginary part of the dielectric constant drops with bias at all temperatures and frequencies. Its peak also moves into the nonpolar region with increasing bias and remains at the same temperature as the peak (or minimum) of the real part of the dielectric constant. An example of this behavior is shown in Fig. 10, which shows the measurements at various biases around the upper Curie temperature made at 8.25 Gc/sec.

Looking at the graphs of the real part of the dielectric constant with their various biases, one can imagine the envelope made up of the maxima to which ϵ' rises with bias at each temperature between the pair of maxima of the unbiased dielectric constant. This envelope is approximately a straight line connecting the two maxima about each Curie temperature in Fig. 3.

The reason for this behavior of the dielectric constant with bias can be understood by repeating the earlier arguments [see Eq. (4)] with differentiation by T replaced by differentiation by E. We then have

$$\frac{\partial\epsilon'}{\partial E}=\frac{\partial\epsilon_0}{\partial E}f(\omega\tau)\left[1+\frac{\partial\ln f(\omega\tau)}{\partial\ln(\omega\tau)}\right]. \qquad (7)$$

The criterion for $\partial\epsilon'/\partial E$ having the opposite sign to $\partial\epsilon_0/\partial E$ (which is always negative) is just the same as that for $\partial\epsilon'/\partial T$ having the opposite sign to $\partial\epsilon_0/\partial T$. The envelope of the curves of ϵ' versus T at various biases, i.e., the curve of the maxima of ϵ' with E as function of T is given by

$$1+\frac{\partial\ln f(\omega\tau)}{\partial\ln(\omega\tau)}=0. \qquad (8)$$

Since Rochelle salt undergoes a Debye relaxation, $f(\omega\tau)=(1+\omega^2\tau^2)^{-1}$. Equation (8) is thus equivalent to $\omega\tau=1$ or $f(\omega\tau)=\frac{1}{2}$. Combining this with Eq. (3) we

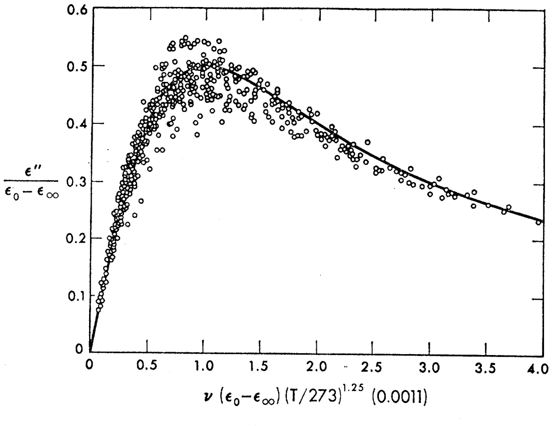

FIG. 9. Imaginary part of normalized dielectric constant of Rochelle salt versus normalized frequency times $(T/273)^{1.25}$. Solid curve is a Debye relaxation function.

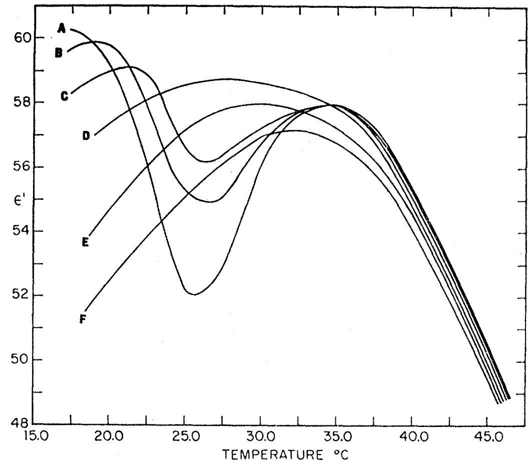

FIG. 10. Temperature dependence of the real part of the dielectric constant at 8.25 GHz of Rochelle salt under various dc biases: (A) no bias; (B) 1.0 kV/cm; (C) 2.0 kV/cm; (D) 4.1 kV/cm; (E) 6.1 kV/cm; (F) 8.2 kV/cm.

obtain the values of ϵ' (which we denote by $\epsilon_{\max}'$) on the envelope as

$$\epsilon_{\max}'-\epsilon_\infty=\tfrac{1}{2}(\epsilon_0-\epsilon_\infty). \tag{9}$$

Thus we find the dependence of τ_0 on $\epsilon_{\max}'$

$$\tau_0^{-1}=2\omega(\epsilon_{\max}'-\epsilon_\infty). \tag{10}$$

Since we have seen that the temperature dependence of the envelope is just given by the slope of the lines connecting the maxima surrounding the Curie points in Fig. 3, we have another method of determining the temperature dependence of τ_0 and thus the explicit temperature dependence of τ. This is not an independent experimental determination, since it only uses the data in Fig. 3 again. It is merely another way of analyzing data, and so it is not surprising that it also yields $\partial \ln\tau_0/\partial \ln T \approx 1.25$ or $\tau \propto (\epsilon_0-\epsilon_\infty)(T/273)^{1.25}$.

Some of these properties of the biased dielectric constant were also observed by Jackle[14] in his measurements at 9.39 Gc/sec in the temperature range from 18 to 40°C and with biases up to 5 kV/cm. He reported that at all temperatures in the above range the real part of the dielectric constant only rises with bias. However, he failed to observe that at the highest biases he used, ϵ' is actually decreasing with bias at all temperatures, and that at the two temperature extremes ϵ' only drops with bias. This drop in ϵ' with bias is essential in establishing the phenomenological relationship that the relaxation time is proportional to the differential value of $\epsilon_0-\epsilon_\infty$.

IV. INTERPRETIVE DISCUSSION

In this section we present a model of the dielectric relaxation in Rochelle salt which is consistent with the experimental observations reviewed in Sec. III. These observations may be summarized briefly as follows:

(1) The frequency dependence of the complex dielectric constant follows a simple Debye relaxation behavior.

(2) The relaxation time is linear in $\epsilon_0-\epsilon_\infty$.

(3) The relaxation time has a small additional *increasing* dependence on temperature, approximately proportional to $T^{5/4}$.

(4) The shape of the relaxation remains a pure Debye relaxation upon polarization and the relaxation time is only slightly polarization-dependent.

The model we develop is basically an extension to high frequencies of the general ideas underlying Mitsui's model for the static ferroelectric behavior of Rochelle salt.[4] For reference we first review some of these ideas. Building upon this structure we make use of the Kubo formulism[19] to obtain a general complex dielectric susceptibility of the requisite character.

Static Model of Ferroelectricity

Mitsui's theoretical model[4] of the polarization of Rochelle salt makes use of a basic assumption taken over from Mason's earlier work on the problem.[6] Mason had suggested that the motion of the ferroelectrically active dipoles is constrained by local, asymmetric, double-well potentials. According to his model, the primary source of ferroelectricity was supposed to be associated with proton motion between two equilibrium positions of a particular set of hydrogen bonds. However, more recent structural evidence throws considerable doubt on the importance of such hydrogen bonds in the ferroelectricity of Rochelle salt.[3,23] Unfortunately, a completely satisfactory structural analysis has yet to be obtained, but neutron diffraction results[24] do suggest that the ferroelectric polarization is, at least partially, associated with the rotation of the hydroxyl groups, denoted $(\mathrm{O\text{-}H})_5$, of the tartrate complex. The protons of the hydroxyl group are apparently free to rotate about the oxygen atoms between two equilibrium positions yielding a net proton displacement component of 1 Å along the ferroelectric direction. There are four such rotatable dipoles per unit cell which can be grouped into two pairs. The protons within each pair are symmetry related even in the ferroelectric region. The pairs themselves are related by symmetry only in the nonpolar states. In Mitsui's model the pairs are assumed to form two interpenetrating sublattices. A representation of the potential energy function of the hydroxyl group is shown schematically in Fig. 11 where the variable x is the projected coordinate in the ferroelectric direction of the proton motion as the hydroxyl group rotates. By

---

[23] G. Shirane, F. Jona, and R. Pepinsky, Proc. I.R.E. **43**, 1738 (1955).

[24] B. C. Frazer, J. Phys. Soc. Japan **17**, Suppl. B-II, 376 (1962).

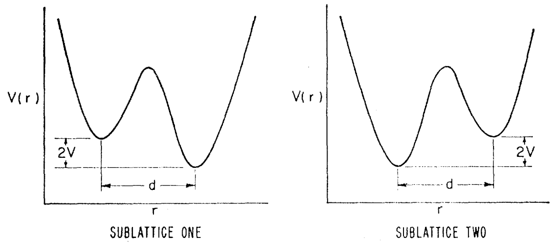

FIG. 11. Assumed asymmetric double-well potential constraining the dipoles responsible for the ferroelectric effect in Rochelle salt.

symmetry requirements, the local potentials for the two sublattices are mirror images of each other.[3,4] Since the two equilibrium positions of the protons are not symmetry related, they would be expected to have different energies. This difference is denoted by $2V$. The motion of the proton corresponds to the reversal of a dipole of moment $\mu=\frac{1}{2}ed$ where d is the component in the ferroelectric direction of the separation of the potential minima. Mitsui assumes that the hydroxyl rotation is the only important atomic rearrangement at the ferroelectric transitions. Recent measurements on the Na^{23} nuclear quadrupole resonance of Rochelle salt[25,26] indicate that this assumption is an over simplification. The atomic motion is probably considerably more complex. However, it seems quite reasonable to accept, at least as a phenomenological device, the notion that the rearrangement is constrained by an asymmetric local potential.

In addition to the local asymmetric potential, Mitsui assumes that the interaction between the ferroelectrically active dipoles may be treated by means of a simple molecular field. It is perhaps surprising to suppose that a molecular-field approach might work at all. As is well known,[27] important transverse correlation effects in dipolar coupled systems make necessary a more Onsager-like[28] treatment of dielectric properties. However, the local potential in Rochelle salt may sufficiently "quench" the transverse components of the electric dipole moment so that transverse correlation would be greatly reduced. In such a case, the longitudinal correlations would dominate and the molecular field would be adequate. The situation would be analogous to that in the magnetic compound dysprosium aluminum garnet.[29,30] In this substance the dominant dipolar interaction may be replaced by an Ising-like interaction, since the dysprosium ion has an extremely anisotropic g factor which leads to a minuscule transverse component of the magnetic dipole moment.

In departure from Mason's theory, Mitsui's model does not assume equal values for the intrasublattice and intersublattice molecular-field constants, denoted, respectively, in his theory by β and β'. It is this view which constitutes Mitsui's crucial contribution to the understanding of the ferroelectricity of Rochelle salt. Unfortunately, at the same time, the mathematical analysis of the problem is greatly complicated by the assumption of two independent molecular-field constants. For our purposes we need not review this analysis in any detail. It is sufficient to note that Mitsui is able to characterize the temperature dependence of the dielectric susceptibility entirely in terms of the relative behavior of two dimensionless parameters viz., $c\equiv(\beta'-\beta)/(\beta'+\beta)$ and $b\equiv N\mu^2(\beta'-\beta)/2V$. In particular, he is able to show that two dielectric singularities or Curie temperatures are possible if $c>0.288$. Thus, Mitsui's model is able to elucidate the most interesting aspect of the ferroelectric of Rochelle salt if $\beta'\neq\beta$. In our subsequent discussion of dynamic behavior we follow only the spirit of Mitsui's model and need not review further its mathematical details.

Dielectric Relaxation Function—Formulism

In an earlier discussion,[22] we analyzed the dielectric relaxation of Rochelle salt in terms of a rather classical model of relaxation towards an "instantaneous equilibrium." In many respects, this discussion follows quite closely the original ideas of Debye[18] and leads directly to the result that the relaxation time varies directly as $(\epsilon_0-\epsilon_\infty)$. Both Mason[6] and Landauer[31] have used a similar kind of analysis in earlier works. As Hill has pointed out,[27] such a treatment is inadequate to account for the dynamic behavior of most polar materials. It completely neglects correlations in the transverse components of the elementary dipole moments. However, as we have pointed out above, the Mitsui model presupposes that the hydroxyl dipole moment has only a single nonvanishing component. Thus, the simple picture may be reasonable for Rochelle salt.

In this paper we would like to make use of the point of view that Kubo and Tomita[19,32] first developed in connection with problems in magnetic resonance. Cole[33] has previously discussed dielectric polarization rather generally in terms of the Kubo formulism. Our work represents a rather specialized extension of his analysis.

If we suppose that $\mathcal{P}$ represents the total polarization operator of a given dielectric material, Kubo has shown quite generally that the complex frequency-dependent, dielectric susceptibility must have the form

$$\chi(\omega)=\Phi(0)-i\omega\int_0^\infty\Phi(t)e^{-i\omega t}dt,\qquad(11)$$

---

[25] R. Blinc, J. Petkovsek, and I. Zupancic, Phys. Rev. **136**, A1684 (1964).

[26] N. C. Miller and P. A. Casabella, Phys. Rev. **152**, 228 (1966).

[27] N. L. Hill, Proc. Roy. Soc. (London) **A240**, 101 (1957).

[28] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[29] D. C. Mattis and W. P. Wolf, Phys. Rev. Letters **16**, 899 (1966).

[30] B. E. Keen, D. Landau, B. Schneider, and W. P. Wolf, J. Appl. Phys. **37**, 1120 (1966).

[31] R. Landauer (private communication).

[32] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[33] R. H. Cole, J. Chem. Phys. **42**, 637 (1965).

where $\Phi(t)$ represents an appropriately defined *relaxation function.* For a canonical statistical ensemble the relaxation function has the form

$$\Phi(t)=\int_0^\beta \langle\mathcal{P}(-i\hbar\lambda)\mathcal{P}(t)\rangle d\lambda-\beta\langle\mathcal{P}_0^2\rangle \tag{12}$$

where $\mathcal{P}_0$ signifies the invariant part of the operator $\mathcal{P}$ with respect to the total Hamiltonian of the system. The operators $\mathcal{P}(t)$ and $\mathcal{P}(-i\hbar\lambda)$ are given, respectively, by $\exp(i\mathcal{H}t/\hbar)\mathcal{P}\exp(-i\mathcal{H}t/\hbar)$ and $\exp(\mathcal{H}\lambda)\times\mathcal{P}\exp(-\mathcal{H}\lambda)$. The bracket notation denotes thermal averages taken with respect to the canonical density matrix $\rho=\exp(-\beta\mathcal{H})/\mathrm{Tr}\exp(-\beta\mathcal{H})$—i.e., $\langle A\rangle=\mathrm{Tr}\rho A$.

In our experiments we are concerned solely with the relaxation of the polarization due to atomic rearrangements at relatively low frequencies well below the relaxation frequencies associated with optical phonons and any correlations in the electronic components of polarization. In this low-frequency case, Eq. (11) may be reduced to

$$\chi_{LF}(\omega)=\chi_\infty-\beta\langle\mathcal{P}_0^2\rangle+\Phi_p(0)-i\omega\int_0^\infty\Phi_p(t)e^{-i\omega t}dt, \tag{13}$$

where

$$\Phi_p=\int_0^\beta\langle P(-i\hbar\lambda)P(t)\rangle d\lambda. \tag{14}$$

The operator P represents the total component of, say, the hydroxyl dipole moments along the ferroelectric axis.

By a formal double integration of the Heisenberg equation of motion, we may obtain the following explicit development of the operator $P(t)$ in terms of the initial operator $P(0)$:

$$P(t)=P(0)+(i/\hbar)\int_0^t dt'[\mathcal{H}(t'),P(0)]$$
$$+(i/\hbar)^2\int_0^t\int_0^{t'}dt'dt''[\mathcal{H}(t'),[\mathcal{H}(t''),P(t'')]]. \tag{15}$$

This development leads us to the following, still exact, expression for the thermal average

$$\langle P(-i\hbar\lambda)P(t)\rangle=\langle P(-i\hbar\lambda)P(0)\rangle$$
$$+(i/\hbar)\int_0^t dt'\langle P(-i\hbar\lambda)[\mathcal{H}(t'),P(0)]\rangle$$
$$+(i/\hbar)^2\int_0^t\int_0^{t'}dt'dt''$$
$$\times\langle[\mathcal{H}(t'),P(-i\hbar\lambda)][\mathcal{H}(t''),P(t'')]\rangle. \tag{16}$$

The particular form of the last term in Eq. (16) is a consequence of the commutation properties of the trace operation. In what follows we shall be concerned only with those Fourier components of Eq. (16) at frequencies less than the frequency associated with the splitting between the two lowest states of the hydroxyl group. Consequently, we may approximate the equation by its behavior over long times. In such a "long time" approximation, we suppose that the time interval t in Eq. (16) is *short* compared to the relaxation time of P, but *long* compared to the characteristic oscillatory periods of $\mathcal{H}_1$ which denotes those parts of the total Hamiltonian not commuting with P. The time is long compared to the correlation times of the microscopic fluctuations in P.

Under these circumstances the second term on the right of Eq. (16) averages out. The integrand of the third term for stationary processes is a function only of the time difference $t''-t'$ and, by assumption, diminishes rapidly. Thus, Eq. (16) has the limiting value

$$\lim_{t\to 0}\langle P(-i\hbar\lambda)P(t)\rangle=\langle P(-i\hbar\lambda)P(0)\rangle+(t/\hbar^2)\int_0^\infty dt'$$
$$\times\langle[\mathcal{H}_1(0),P(-i\hbar\lambda)][\mathcal{H}_1(t'),P(t')]\rangle. \tag{17}$$

It is not unreasonable to identify this approximation with the first two terms of the series expansion of a Debye relaxation function $\Phi_p(t)=\Phi_p(0)\exp(-t/\tau)$. According to this identification the relaxation time would be given by

$$\tau^{-1}=-\left\{\int_0^\beta d\lambda\int_0^\infty dt\langle[\mathcal{H}_1(0),P(-i\hbar\lambda)]\right.$$
$$\left.\times[\mathcal{H}_1(t),P(t)]\rangle\right\}\left\{h^2\int_0^\beta d\lambda\langle P(-i\hbar\lambda)P(0)\rangle\right\}^{-1} \tag{18}$$

or from Eqs. (13) and (14):

$$\tau^{-1}=-\left\{\int_0^\beta d\lambda\int_0^\beta dt[\mathcal{H}_1(0),P(-i\hbar\lambda)][\mathcal{H}_1(t),P(t)]\right\}$$
$$\times\{\hbar^2[(\chi_0-\chi_\infty)+\beta\langle\mathcal{P}_0^2\rangle]\}^{-1}. \tag{19}$$

A Debye relaxation is, thus, reasonable in the *long time* approximation used here. Equations (18) and (19) are similar in content to expressions developed by Mori and Kawasaki[34] for the relaxation time of a Heisenberg ferromagnet. In the "classical" limit $\hbar=0$, Eq. (19) takes on a particularly simple form

$$\tau^{-1}=\left\{\int^\infty\langle P(0)P(t)\rangle dt\right\}\{kT[\chi_0-\chi_\infty]+\langle\mathcal{P}_0^2\rangle\}^{-1}. \tag{20}$$

If the numerator in this expression is a weak function of the temperature, the predicted temperature dependence of τ is quite consistent with the previously discussed experimental results, viz., $\tau\propto T(\epsilon_0-\epsilon_\infty)$. The term $\langle\mathcal{P}_0^2\rangle$ in the denominator of Eq. (20) is negligible. Using Hablutzel's values[35] for the saturation polarization we find this term to be less than 0.1% of $kT(\chi_0-\chi_\infty)$ even in the middle of the ferroelectric range. As we

---

[34] H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962).

[35] J. Hablützel, Helv. Phys. Acta. **8**, 489 (1935).

show in the next section, the numerator of Eq. (20) would be expected to have a weak temperature variation if the time dependence of P is due mainly to one phonon transitions between the two lowest states of the hydroxyl ions.

Model Hamiltonian of Polarization Mechanism

In order to obtain a little more physical insight into the significance of Eq. (20), we present a greatly oversimplified picture of the dynamics of the proton or hydroxyl ion moving in an asymmetric double potential well, such as depicted in Fig. 11. Following a suggestion of de Gennes,[36] we construct by means of the Pauli spin matrices, a model Hamiltonian of the lowest states of a dipole coupled system within which individual particles move in asymmetric double wells. We assume that there are two distinct sublattices characterized by the sense of asymmetry of the individual double wells. The expectation value of the Pauli operator $\sigma_{\alpha i}{}^{z}$ is taken as a measure of the degree of a particle localization on a particular side of the double well at the ith site of the αth sublattice. The sum of $\sigma_{\alpha i}{}^{z}$ over all sites and both sublattices constitutes a representation of an operator proportional to the total polarization operator P. To adequately model our problem our Hamiltonian must contain five distinct types of terms—viz.,

$$\mathcal{H}=\sum_{\alpha,i}K_i{}^{\alpha}(\sigma_{\alpha i}{}^{z})^2+\sum_{\alpha,i}V_i{}^{\alpha}\sigma_{\alpha i}{}^{z}+\sum_{\alpha,i}T_i{}^{\alpha}\sigma_{\alpha i}{}^{x}-E\mu\sum_{\alpha,i}\sigma_{\alpha i}{}^{z}+\sum_{\alpha,i}\sum_{\beta,j}J_{ij}{}^{\alpha\beta}\sigma_{\alpha i}{}^{z}\sigma_{\beta j}{}^{z}. \quad (21)$$

The first two terms represent the individual energies of two separated asymmetric potential wells. According to the Mitsui model, the static, unpolarized Rochelle salt lattice would have $V_i{}^{1}=V^{1}=-V^{2}$. These two terms alone lead to eigenstates which describe a particle motion localized about the minimum in a particular well. The third term in Eq. (23) represents the nonlocalization effect produced by the proximity of the two sides of the double well. The fourth term is just the electrostatic interaction between the individual dipoles and the local electric field E. The fifth term is an Ising representation of the inter-protonic dipolar interaction. As we have said before, the Ising approximation is probably adequate here since the hydroxyl ions are assumed to have only one definite component of local dipole moment. Equation (21) would reproduce identically the static behavior discussed in Mitsui's model.

In view of our simple model Hamiltonian, Eq. (20) takes on the following specific form:

$$\tau^{-1}=(4\mu^2/\hbar^2)\left[\sum_{\alpha,i}\sum_{\beta,j}\int_0^{\infty}\langle T_i{}^{\alpha}(0)\,T_j{}^{\beta}(t)\,\sigma_{\alpha i}{}^{y}(0)\,\sigma_{\rho j}{}^{y}(t)\rangle dt\right][kT(\chi_0-\chi_\infty)]^{-1}. \quad (22)$$

In general, we would not expect fluctuations in the lattice potential parameters $T_i{}^{\alpha}$ to be correlated with the fluctuations in the protonic motion. Thus, we may factorize the numerator of Eq. (22) as

$$\int_0^{\infty}\langle T_i{}^{\alpha}(0)\,T_j{}^{\beta}(t)\,\sigma_{\alpha i}{}^{y}(0)\,\sigma_{\beta j}{}^{y}(t)\rangle dt=\int_0^{\infty}\langle T_i{}^{\alpha}(0)\times T_j{}^{\beta}(t)\rangle\langle\sigma_{\alpha i}{}^{y}(0)\,\sigma_{\beta j}{}^{y}(t)\rangle dt. \quad (23)$$

In a pure Ising model, of course, there is no cross correlation between the transverse "spin" components from site to site. However, the "tunneling" or nonlocalizing effect of the $\sigma_{\alpha i}{}^{x}$ terms in Eq. (21) gives rise to some transverse cross correlation. In our problem the cross correlation leads to a relaxation mechanism similar to *cross relaxation* in magnetic resonance. Such mechanisms would be essentially temperature independent. For simplicity, we neglect these cross-correlation effects by assuming that the eigenstates of the system are fairly well localized on either side of the potential barrier. Thus, we assume that

$$\langle\sigma_{\alpha i}{}^{y}(0)\,\sigma_{\beta j}{}^{y}(t)\rangle=\delta_{\alpha\beta}\delta_{ij}\langle\sigma_{\alpha i}{}^{y}(0)\,\sigma_{\alpha i}{}^{y}(t)\rangle. \quad (24)$$

This self-correlation function has only Fourier components at zero frequency and at the frequencies $\Delta E_\alpha/h$ where ΔE_α is the splitting between the two lowest states of the protons on the αth sublattice. The lattice vibrations lead to modulations of the tunneling integral $T_i{}^{\alpha}$ which lead in turn to direct transitions between the protonic levels. The relevant Fourier components of $\langle T_i{}^{\alpha}(0)\,T_i{}^{\alpha}(t)\rangle$ vary as the average lattice displacement at the frequency $\Delta E_\alpha/\hbar$—i.e., as $\rho(\Delta E_\alpha)\coth(\Delta E_\alpha/2kT)$ where $\rho(\Delta E_\alpha)$ is the density of phonon states of energy ΔE_α.

For the direct one-phonon relaxation process we may then write

$$\tau^{-1}=(4\mu^2/\hbar^2)\Big[\sum_{\alpha}G_\alpha\,|\,\langle e_\alpha\,|\,\sigma_\alpha{}^{y}\,|\,g_\alpha\rangle\,|^2\times\rho(\Delta E_\alpha)\coth(\Delta E_\alpha/2kT)\Big][kT(\chi_0-\chi_\infty)]^{-1}. \quad (25)$$

In this expression $|\,g_\alpha\rangle$ and $|\,e_\alpha\rangle$ represent, respectively, the ground and first excited protonic states. The parameter G_α is proportional to the square of appropriate strain derivatives of the tunneling integral. For $\Delta E_\alpha > 2kT$ the factor coth $(\Delta E_\alpha/kT)$ is essentially temperature-independent and Eq. (25) is consistent with experimental observation. However, ΔE_α must also be larger than kT to explain the static behavior of the system. The slight deviations from Eq. (5) in the ferroelectric region might be associated with small changes in the splittings ΔE_α in this region.

---

[36] P. G. de Gennes, Solid State Commun. **1**, 132 (1963).

V. CONCLUSIONS

By means of the Kubo formalism for generalized susceptibilities, we have shown that the experimentally observed frequency variations in the complex dielectric constant of Rochelle salt are consistent with the spirit of Mitsui's model of static behavior. Experimentally, the frequency variations are found to be strictly Debye in character. Such a Debye relaxation behavior is reasonable if we assume that the dominant dielectric relaxation mechanism is associated with rapid modulations of the local potentials at the sites of the ferroelectrically active dipoles. In these circumstances, the temperature dependence of the macroscopically observed relaxation time should be dominated by the effects of long-range correlations which give rise to the experimentally observed $T(\epsilon_0-\epsilon_\infty)$ variations in the Debye relaxation time.

PHYSICAL REVIEW VOLUME 168, NUMBER 2 10 APRIL 1968

Closed-Form Solution for the Collective Bound State due to the *s-d* Exchange Interaction

AKIO YOSHIMORI
Institute for Solid State Physics, University of Tokyo, Tokyo, Japan

(Received 6 September 1967)

A closed-form solution is derived to an integral equation for the singlet collective bound state, which has been shown by Yosida to be the ground state of a system of conduction electrons coupled with a single localized spin due to the antiferromagnetic *s-d* exchange interaction. The solution is valid to logarithmic accuracy, with an assumption concerning a series in the equation. The triplet collective bound state is also examined, and no solution is found.

THEORIES have been developed by many authors in various approaches to the problem of the low-temperature anomaly, considered by Kondo, in a system of conduction electrons coupled with a single localized spin by the *s-d* exchange interaction.[1–11] Among these, Yosida[8] has shown, by a generalized perturbation method, for the case of the antiferromagnetic exchange interaction, that the ground state of this system is a singlet collective bound state, in which the spin is quenched. (This paper will be referred to as I.) This conclusion has been confirmed by Okiji through a higher-order calculation.[9] The energy of this singlet state has been shown to be lower by the binding energy $-\tilde{E}$ than that of the normal state calculated by the usual perturbation method.[10] In this paper a closed-form solution to an integral equation for the collective bound state is derived on the basis of the theory by Yosida in I. The solution is valid in logarithmic accuracy and with an assumption concerning a series in the equation.

The eigenfunction for the collective bound state is constructed in I as follows:

$$\begin{aligned}\psi=\{\sum_k\,&[\Gamma_k{}^\alpha a_{k\downarrow}{}^\dagger\alpha+\Gamma_k{}^\beta a_{k\uparrow}{}^\dagger\beta]\\&+\sum_{k_1k_2k_3}[\Gamma_{k_1k_2k_3}{}^{\alpha\downarrow}a_{k_1\downarrow}{}^\dagger a_{k_2\downarrow}{}^\dagger a_{k_3\downarrow}\alpha+\Gamma_{k_1k_2k_3}{}^{\beta\uparrow}a_{k_1\uparrow}{}^\dagger a_{k_2\uparrow}{}^\dagger a_{k_3\uparrow}\beta\\&+\Gamma_{k_1k_2k_3}{}^{\alpha\uparrow}a_{k_1\downarrow}{}^\dagger a_{k_2\uparrow}{}^\dagger a_{k_3\uparrow}\alpha+\Gamma_{k_1k_2k_3}{}^{\beta\downarrow}a_{k_1\uparrow}{}^\dagger a_{k_2\downarrow}{}^\dagger a_{k_3\downarrow}\beta]\\&+\cdots\}\psi_v,\end{aligned}\tag{1}$$

where α and β denote, respectively, the up and down spin states for the localized spin $(S=\frac{1}{2})$, and ψ_v denotes the Fermi state. From the Schrödinger equation an infinite chain of integral equations for Γ_k, $\Gamma_{k_1k_2k_3}$, and coefficients of higher-order terms, is derived.[8,9] In these equations one can express $\Gamma_{k_1k_2k_3}$ in terms of Γ_k, and successively each higher-order coefficient in terms of the next lower-order one, to eliminate higher-order coefficients, following Yosida and Okiji.[8,9] These equations are finally reduced to integral equations for $\Gamma_k{}^\alpha$ and $\Gamma_k{}^\beta$ only.

Putting $\Gamma_k{}^\alpha=-\Gamma_k{}^\beta=\Gamma(\epsilon_k)$ for the singlet state as in I, and replacing summations over k by integrations with the band energy ϵ on the assumption of the constant density of states ρ for $-D\leq\epsilon\leq D$ (ϵ is measured from the Fermi energy), one finds the integral equation

---

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[2] H. Suhl, Phys. Rev. **138**, A515 (1965); H. Suhl and D. Wong, Physics **3**, 17 (1967).
[3] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965); Progr. Theoret. Phys. (Kyoto) **37**, 13 (1967).
[4] A. A. Abrikosov, Physics **2**, 5 (1965).
[5] D. R. Hamann, Phys. Rev. **158**, 570 (1967).
[6] J. Kondo, Phys. Rev. **154**, 644 (1967).
[7] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 505 (1965).
[8] K. Yosida, Phys. Rev. **147**, 223 (1966).
[9] A. Okiji, Progr. Theoret. Phys. (Kyoto) **36**, 712 (1966).
[10] K. Yosida, Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966).
[11] H. Ishii and K. Yosida, Progr. Theoret. Phys. (Kyoto) **38**, 61 (1967).