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THE DIELECTRIC PROPERTIES OF BARIUM TITANATE
AT LOW TEMPERATURES

by

Robert F. Blunt

A thesis presented to the faculty of The Rice Institute
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

The Rice Institute
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ABSTRACT

Measurements of the complex dielectric constant of ceramic barium titanate have been made at temperatures ranging from 300°K down to 2.4°K . The frequencies employed ranged from 50 kilocycles per second up to 2 megacycles per second with the majority of the measurements at 500 kilocycles per second. The real part of the dielectric constant, K' , had a value of about 1100 at room temperature, decreasing to approximately 100 in the liquid helium temperature region ($2-4^{\circ}\text{K}$). The slope of K' against the temperature had a high positive value of 0.01 per $^{\circ}\text{K}$ in agreement with Wul⁽¹⁾. The imaginary part of the dielectric constant, K'' , had a value of about 4 at room temperature, rising to a very broad maximum of

approximately 15 at 200°K and steadily decreasing below 80°K to room temperature values below 4 in the liquid helium region. The experimental work was done in the Collins cryostat of the low temperature laboratory of The Rice Institute, and the impedance measurements were made with a Boonton Q-meter and a General Radio Type 916-A impedance bridge. In addition to the pure barium titanate measurements, measurements were also made on specimens diluted with 15% and 30% strontium titanate respectively. The curves obtained for diluted specimens had the same general appearance as those for the pure barium titanate except that the sharp maximum in the K' curve, normally occurring at 390°K, was brought near room temperature in case of the 15% dilution and to 274°K for the 30% dilution. This lowering of the temperature of the peak is in accord with results reported by von Hippel⁽²⁾, Coursey and Brand⁽³⁾, and Jackson and Reddish⁽⁴⁾.

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THE DIELECTRIC PROPERTIES OF BARIUM TITANATE
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I. INTRODUCTION

The experimental investigation described below was initiated at the low temperature conference sponsored by the National Academy on Shelter Island on June 5, 1948. It took the form of a request from J. M. Richardson of the Bell Telephone Laboratories for measurements on the dielectric constant of ceramic barium titanate at low temperatures with particular emphasis on the 2-5°K region. Richardson wished for us to verify the large slope in the dielectric constant vs. temperature curve at low temperatures reported by Wul^[1]. This we succeeded in doing last September, but in so doing we discovered a very interesting peak in the $\tan \delta$ vs. temperature curve. Because of this latter, the work has continued beyond the initial program proposed. Additional low temperature runs on pure ceramic barium titanate have

been made to study the complex dielectric constant at temperatures ranging all the way from 300°K down to the $2-5^{\circ}\text{K}$ region.

Finally, at a conference with Richardson at the Bell Laboratories in February 1949, it was decided to make measurements on solid solutions consisting of barium titanate diluted with 15% and 30% strontium titanate respectively. These latter measurements were made in an effort to see if the dilution with a material of much lower dielectric constant would cause the temperature slope to become zero at temperatures above 2°K . It was felt that if a zero slope was effected, valuable information as to the origin of the high slope at low temperature observed in pure barium titanate as well as the more general remarkable dielectric properties of barium titanate might be obtained. However, all specimens, pure and dilute, showed approximately the same slope at low temperatures, approximately 0.01 per degree Kelvin.

In order to discuss the dielectric properties of barium titanate, it would seem very worth while to give a brief account of dielectric properties in general, the mechanisms causing them, and in short ~~to define~~ the term "complex dielectric constant".

If an electric field is applied to a system of bound

charges, the charges are displaced creating electric dipole moments which increase the resultant field. This is generally expressed as

$$D = \epsilon_0 K E = \epsilon_0 E + P ,$$

where D is the electrical displacement, ϵ_0 the permittivity of free space, E the electric field, and P the dipole moment per unit volume. K is the dielectric constant which depends on the polarization P where P is given by $P = \sum ex$ and where e is the charge, x the displacement, and the summation is taken over all charges in a unit volume. P can also be expressed as $P = \chi E$ where χ is the volume polarizability of the bulk material. P , E , and x are vector quantities such that P and E are not necessarily parallel. For isotropic materials P is a linear function of E , while for anisotropic materials P is a linear vector function of E .

There may also be free charges which give rise to conduction current. The conductivity of the ceramic barium titanate is so small that it will be neglected here, except for the brief mention of interfacial polarization which can be considered as follows.. In an inhomogeneous substance one has regions with different dielectric constants and different conductivities which can result in the collection

of free charges at the interfaces between the regions. This is equivalent to additional polarization and hence an apparent dielectric constant higher than one would get by merely considering the polarization of the bound charges responsible for the dielectric constants of the individual layers.

One other source of resultant polarization exists, - namely, that caused by the presence in the material of permanent electric dipole moments. These can either be in the form of polar molecules or certain kinds of ionic crystals. Both satisfy the requirement of assymetry in electrical charges which gives a resultant electric dipole moment. If we consider a dielectric material as consisting of large numbers of dipoles oriented at random, an applied electric field will serve to line these up, giving a resultant polarization. In this case thermal collisions give an effective restoring torque which makes the resultant polarization dependent on the applied field. The polarization in ionic crystals will be discussed later in conjunction with the ferro electric properties of barium titanate.

So far nothing has been said about periodic electric fields. Bound charges, of course, have natural resonant frequencies that can be excited by periodic electric fields. At zero frequency or at frequencies well below the natural frequency the charge displacement is able to follow the

applied field exactly, in phase with it and having an amplitude that can be calculated directly from the restoring force constant and the field. Thus for low frequencies one would expect to get a polarization, $P = \epsilon_0 E$, and dielectric constant K from $\epsilon_0 K E = \epsilon_0 E + P$ with both K and P in phase with E and such that both are independent of frequency. On the other hand, if the applied frequency is much higher than the resonant frequency of the bound charges, there is negligible displacement and polarization. That is $K = 1$. For the intermediate frequency region, which will be discussed in more detail later, one gets a displacement and hence a polarization and a dielectric constant that is frequency dependent. This is the phenomena of dispersion.

There remains the problem of damping or friction. For periodic fields the damping term causes a phase lag in the polarization which results in energy dissipation as will be seen presently. This loss will show up as an imaginary component in the dielectric constant making the dielectric constant complex. We have in this case $K = K' - iK''$, where K is the complex dielectric constant of which K' and K'' are respectively the real and imaginary parts. The complex dielectric constant K will henceforth be used in the manner defined above.

Several types of bound charges cause polarization.

Electrons have natural resonant frequencies in the visible and ultraviolet region; molecular vibrations lie largely in the infra-red. The "restrahlen" frequencies of the ions in crystals likewise are in the infra-red. Each of these mechanisms often manifests itself in more than one resonant frequency. Thus at any given frequency, a dielectric material has a dielectric constant, K , resulting from the contributions of many oscillators. If we examine the entire frequency spectrum from zero frequency to optical frequencies, we find a general decrease in the real part of the complex dielectric constant K' as the resonant frequency of each type of oscillator is exceeded. Further discussion can best be made by the examination in detail of the following idealized system.

We shall assume a uniform distribution of equal bound charges having elastic restoring forces and a damping force proportional to the velocity of the charges. The equation of motion of one of these charges is

$$(1) \dots m \ddot{x} + r \dot{x} + f x = e E,$$

where m is the mass of the charge, e the value of the charge, r a damping coefficient, f the restoring force constant, and E the internal electric field actually applied to the charge. We assume for the moment that E is

identical with the field applied to the bulk dielectric.

Let E be periodic, that is $E = E_0 e^{i\omega t}$. Then it follows that the steady state solution of equation (1) is just

$$x = \alpha E \quad \text{where } \alpha = \frac{e}{ir\omega - m\omega^2 + f}$$

$$\text{or } x = \frac{e/m E}{(\omega_0^2 - \omega^2) + i r \omega / m} \quad \text{defining } \omega_0 = \sqrt{f/m}$$

and where ω_0 is the natural resonant frequency of the harmonic oscillator

$$m \ddot{x} + f x = 0.$$

If we have N charges per unit volume, the polarization of the bulk material is

$$P = \sum^N e x = \frac{Ne^2/m}{(\omega_0^2 - \omega^2) + i r \omega / m} E.$$

And from the well known relation $D = \epsilon_0 E + P = \epsilon_0 K E$

$$\text{we can write (2).... } \epsilon_0 K E = \epsilon_0 E \left(1 + \frac{Ne^2/m\epsilon_0}{(\omega_0^2 - \omega^2) + i r \omega / m} \right)$$

$$\text{or simply (3).... } K = K' - i K'' = 1 + \frac{Ne^2/m\epsilon_0}{(\omega_0^2 - \omega^2) + i r \omega / m}.$$

Since we will be dealing exclusively with non-magnetic materials, the optical index of refraction is given by

$$(4).... (n - i k)^2 = K$$

where n is the principle index of refraction and k the absorption coefficient. Energy dissipation is to be expected because of the inclusion of the damping term in equation (1).

The dependence of K or n on frequency is termed dispersion which can be discussed as follows. For very low frequencies where $\omega \ll \omega_0$, $i r\omega/m$ and ω^2 are negligible in equation (3),

$$\text{thus } K = n^2 = 1 + \frac{N e^2 / m \epsilon_0}{\omega_0^2}.$$

This is the static value of the dielectric constant. If lies in the optical frequency range such that for any practical problem $n \sim 1$, then if ω is still sufficiently removed from ω_0 to make $i r\omega/m \ll (\omega_0^2 - \omega^2)$

$$\text{we have } n - 1 = 1/2 \frac{N e^2 / m \epsilon_0}{\omega_0^2 - \omega^2}.$$

This makes n increase as the frequency increases; this type of frequency dependence is the normal dispersion. Near the resonant frequency of

the oscillators the damping term becomes important, and we get the so called anomalous dispersion.

From equation (2) we can get, assuming $n \sim 1$,

$$n - 1 \approx \frac{1}{2} \frac{N e^2 / m \epsilon_0}{(\omega_0^2 - \omega^2) + i r \omega / m}$$

or simply (5).... $n - 1 = \frac{1}{2} \frac{N e^2}{m \epsilon_0} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + r^2 \omega^2 / m^2},$

and (6).... $k = \frac{1}{2} \frac{N e^2}{m \epsilon_0} \cdot \frac{r \omega / m}{(\omega_0^2 - \omega^2)^2 + r^2 \omega^2 / m^2}.$

From the form of equation (5) we see that $n - 1$ is zero at $\omega = \omega_0$ and has a positive peak below and a negative peak above ω_0 such that in the region between these peaks, $n - 1$ decreases with increasing frequency. For historical reasons this is now inaptly called anomalous dispersion.

Similarly equation (6) gives a single peak in k with its maximum near ω_0 .

In optical phenomena anomalous dispersion is not generally observed because of the absorption band resulting from the maximum given by (6), whereas the so called anomalous

dispersion is found in K almost universally for all frequencies from zero up to the highest radio frequencies.

It was assumed earlier in equation (1) that the force on the charges was given by assuming the internal electrical field to be the same as the applied external field. This is not true, of course, in any case where the polarization P is sufficient to give appreciable additional local fields to individual charges. Thus the internal field actually applied to a single oscillator is greater than the field applied to the bulk dielectric. This augmentation is certainly of importance in the case of solid dielectrics having high dielectric constants.

Let us consider the single case of an isotropic medium where the approximate Lorentz expression is

$$E_i = E + \frac{4\pi P}{3} \quad . \quad \text{We can then write}$$

equation (1) as

$$m \ddot{x} + r \dot{x} + f x = e \left(E + \frac{4\pi P}{3} \right), \text{ and}$$

from the definition $P = \sum^N e x$ we get

$$m \ddot{P} + r \dot{P} + f P = N e^2 \left(E + \frac{4\pi P}{3} \right) \text{ where}$$

N is again the number of charges per unit volume,

$$\text{or} \quad m \ddot{P} + r \dot{P} + \left(f + \frac{4\pi P}{3} N e^2 \right) P = N e^2 E.$$

If we now define $\bar{\omega}_0^2 = \omega_0^2 - \frac{4\pi N e^2}{3 m}$ which is the

square of the frequency of the oscillator

$$m \ddot{P} + (f - 4\pi/3 \cdot N e^2) P = 0,$$

we can immediately write the new form of equation (3),

$$(7) \dots K = K' - i K'' = 1 + \frac{N e^2 / m \epsilon_0}{(\bar{\omega}_0^2 - \omega^2) + i r \omega / m},$$

such that

$$(8) \dots K' = 1 - \frac{N e^2}{m \epsilon_0} \cdot \frac{\bar{\omega}_0^2 - \omega^2}{(\bar{\omega}_0^2 - \omega^2)^2 + r^2 \omega^2 / m^2},$$

$$\text{and} \quad (9) \dots K'' = \frac{N e^2}{m \epsilon_0} \cdot \frac{r \omega / m}{(\bar{\omega}_0^2 - \omega^2)^2 + r^2 \omega^2 / m^2}.$$

And finally to K' and K'' we must add a much used derived quantity

$$(10) \dots \tan \delta = K''/K' .$$

To give further physical meaning to K' and K'' , and at the same time to show the relationship existing between them and the more familiar electrical terms, we consider the following.

$$\text{From } \epsilon_0 K E = \epsilon_0 E + P \quad \text{or} \quad P = \epsilon_0 E (K - 1) \quad \text{and}$$

$$P = \sum e x = N e x \quad \text{we write the charge displacement } x \quad \text{as}$$

$$x = \frac{\epsilon_0 E (K - 1)}{N e} . \quad \text{If we write the complex dielectric}$$

constant K as $K = /K/ e^{-i\delta}$ and let the applied field

$$\text{be } E = E_0 e^{i\omega t}, \quad \text{we get}$$

$$x = \frac{\epsilon_0 E_0 e^{i\omega t}}{N e} (/K/ e^{-i\delta} - 1) = \frac{\epsilon_0 E_0}{N e} (/K/ e^{i(\omega t - \delta)} - e^{i\omega t}) .$$

The energy dissipation per unit volume per second is given by

$$W = N \omega \int E_i e \, dx \quad \text{where } \omega \text{ is the frequency,}$$

$$E_i = E + \frac{4\pi P}{3}, \text{ and the integral is to be taken}$$

over one period. Substituting for E_i and for x and integrating, we find that

$$W = \frac{\epsilon_0 \omega E_0^2 /K/ \sin \delta}{2}, \text{ or just}$$

$$(11) \dots W = \frac{\epsilon_0 \omega E_0^2 K''}{2} \text{ since}$$

$$K = K' - iK'' = /K/e^{-i\delta}, \text{ and } K'' = /k/\sin \delta.$$

We can get W in terms of familiar electrical terms by considering a parallel plate condenser consisting of two plates a distance d apart, each of area A . We make d/A so small that edge effects are negligible and let the dielectric constant be $K = K' - i k''$. If we assume as the equivalent circuit a perfect lossless condenser of capacity C in parallel with a resistance R , we can calculate W .

$$\text{From the relation } h = \frac{d}{\epsilon_0 A}, \text{ where } \epsilon_0 \text{ is the}$$

specific conductivity at the frequency ω , the energy

dissipation per unit volume is given by $W = E^2 \sigma = \frac{E_0^2 \sigma}{2}$.

Comparing this with the equation (11), we see that

$$K'' = \frac{\sigma}{\omega \epsilon_0}.$$

The familiar capacity formula for a parallel plate condenser,

$$C = \frac{\epsilon_0 K A}{d} \quad \text{shows us at once that the}$$

real part of the complex dielectric constant $K = K' - i K''$ is to be identified with the capacitance formula above.

II. THE DIELECTRIC PROPERTIES OF TITANIUM COMPOUNDS

The ionic crystal lattice becomes polarized by means of the displacement of ions from their equilibrium positions. The electric dipole moments so created appear macroscopically as the polarization P , the dipole moment per unit volume. For most ionic crystals, the real part of the complex dielectric constant, K' , is low, a fact explained by the relatively tight binding of the ions. As dielectric materials they have a low $\tan \delta$. Certain titanium compounds, on the other hand, have high values of K' .

During the late war considerable study of the dielectric properties of titanium dioxide and the alkaline earth titanates was made in Russia, England, and this country. This was done for the very practical purpose of finding high dielectric constant low loss dielectrics, and naturally was not very widely publicized during the war for security reasons. Since then a great deal has appeared in the literature on the subject.

A. von Hippel and his group at the Laboratory for Insulation Research, Massachusetts Institute of Technology² studied a number of the compounds in the form of ceramics. Titanium dioxide has a K' of about 100 at room temperature with a negative temperature coefficient of about - 0.094 per degree centigrade. $\tan \delta$ was less than 0.001 from 150 K° up to room tem-

perature, rising sharply at higher temperatures. K' likewise began to rise above room temperature. At room temperature K' had a slight negative slope for frequencies ranging from low audio up to 100 megacycles per second. $\tan \delta$ showed high values at low audio frequencies decreasing at higher frequencies to a constant value of 0.0003 at radio frequencies. This latter value is only slightly higher than that deduced from infra-red reflection coefficient measurements. These results are in substantial agreement with those reported by Berberich and Bell⁵.

Magnesium titanate, calcium titanate, and strontium titanate showed generally the same characteristics except for the positive temperature coefficient of K' in magnesium titanate ^{and except} for different magnitudes of K' . Magnesium titanate for example had a K' of only about 14 at room temperature, while the other titanates mentioned had K' in the order of several hundreds. Barium titanate was remarkably different; it had an extremely high peak of 6500 at 390° K with sharply decreasing values for lower and higher temperatures, being about 1100 at room temperature and decreasing with decreasing temperature down to 150°K. $\tan \delta$ was somewhat higher for barium titanate than for the other compounds listed, showing for audio frequencies a high peak of 0.06 near 273°K, decreasing to low values at 150°K.

Von Hippel also reported measurements on the solid solutions consisting of 75% BaTiO_3 plus 25% SrTiO_3 and 71% BaTiO_3 plus 29% SrTiO_3 . For these he found that the peak in K' had been shifted to lower temperatures, with no appreciable change in the $\tan \delta$ for audio frequencies. This shift in the K' maximum to lower temperatures depends on the amount of dilution with SrTiO_3 giving a decrease to 280°K for the 29% dilution. This is in agreement with the results reported by Coursey and Brand³ and Jackson and Reddish⁴, who found that the temperature corresponding to the maximum K' varied linearly with the percentage dilution with SrTiO_3 such that solid solutions of 20% BaTiO_3 plus 80% SrTiO_3 had a K' maximum at 73°K as compared with 390°K for the pure BaTiO_3 . Even more remarkable, the values of the maximum K' , about 6500, was not changed appreciably with dilution, even down to solutions of only 20% BaTiO_3 in spite of the relatively low values for pure SrTiO_3 (about 400).

Static measurements of the K' of BaTiO_3 made by von Hippel² show the maximum in K' at 390°K but show in addition definite maximums near 170°K and 270°K . These are sometimes seen in dynamic measurements, appearing usually as small breaks in the otherwise smoothly decreasing K' curve as the temperature decreases.

Wul¹ likewise made a systematic study of K' only for the alkaline earth titanates. He observed that the room tempera-

ture value K' increased with the increasing ion size of the alkaline earth ions, giving the following results:

	Alkaline Earth	Crystal Structure	K' (room temp.)
Odd Series	Mg	Hexagonal	17
	Zinc	--	30
	Cd	Hexagonal	62
Even Series	Be	--	70
	Ca	Cubic	115
	Sr	Cubic	155
	Ba	Cubic	1000

Most interesting of all, he made measurements on ceramic BaTiO_3 down to 2°K , finding that K' had decreased to about 100 at this temperature and had a high positive slope of 0.06 per degree Kelvin in the liquid helium temperature region ($2-4^\circ\text{K}$). This latter was regarded by Wul as quite high in view of the third law of thermo-dynamics from which it is expected that such properties of matter as the dielectric constant would have zero temperature slope at 0°K .

It is generally believed that the high values of K' existing in the titanium compounds is due to the loose binding of the Ti ion in the unit crystalline cell. Loose binding would permit large displacements of the Ti ion, and hence

the high values of K' observed.

In the study of TiO_2 and the titanates which have K' with negative temperature slopes, the possibility of expansion accounting for the temperature dependence immediately suggests itself. From equation (8) we have in form

$$K' - 1 = N/V \bar{\mu}$$

where N is the number of dipoles per unit volume, $\bar{\mu}$ the average moment per dipole, and V the unit volume at any given temperature. It follows then that

$$dK'/dT = (K' - 1) \left(\frac{1}{\bar{\mu}} \frac{d}{dT} - \frac{1}{V} \frac{dV}{dT} \right).$$

If $\bar{\mu}$ were temperature independent, dK'/dT would be explained by the observed positive thermal coefficient of expansion. However, von Hippel² found that in the case of TiO_2 , CaTiO_3 , and SrTiO_3 , the observed value of dK'/dT is ten times or more greater than that calculated from the thermal expansion coefficient. MgTiO_3 , on the other hand, has a positive temperature coefficient in K' in spite of the positive expansion coefficient; thus it is quite apparent that the average dipole moment is strongly dependent on temperature for the above materials.

In barium titanate von Hippel found a small expansion coefficient, which of course does not explain its remarkable dielectric properties but he did note two breaks in the expansion coefficient, one near 273°K and one near 390°K . The dilution with 25% and with 29% strontium titanate did not shift the break near 273°K but shifted the second break to lower temperatures which coincided with the new positions of the steep maximum in K' .

Below 390°K the unit crystalline cell of barium titanate is approximately cubic and consists of an octahedral TiO_6 group in the center of a cube formed by six barium ions at the corners of the unit cell, the six oxygen ions occupying the faces of the cube. It has been suggested that the large barium ions distort the octahedral group in such a way as to give the central Ti ion more room in which to move. Hence loose binding results. This would be in keeping with the observed increase in K' as the size of the alkaline earth ion increases. X-ray powder diffraction studies made by Megaw⁶ and Danielson⁷ reveal that the unit crystalline cell is not truly cubic but tetragonal with the Ti ion shifted from its normal central position towards one of the oxygen atoms on the face of the cube. The unit cell is elongated in the direction of motion of the Ti ion about 1%, while the other dimensions of the unit cell are shortened by half this amount so as to keep the volume constant. (The direction of elongation

is the optical or c axis, the a axis being the directions perpendicular to the other faces of unit cell.) The elongation is only about $1\frac{1}{2}\%$ of the normal $4 \text{ \AA}$. Above 393°K the tetragonal form goes into the cubic.

The permanent dipole moment of the unit cell below the transition point suggests the possibility of a resultant macroscopic polarization. As it turns out, the structure of ceramic barium titanate discussed so far consists of small crystals, each of which is made up of one or more domains. These domains are analogous to the ferromagnetic domains in iron to the extent of having large permanent electric dipole moments. Each domain has all of its dipoles lined up, giving a large dipole moment per unit volume. The domains have random orientation, so the resultant macroscopic polarization in a zero external electric field is generally zero. Many workers have found that K' for the ceramic material depends on the magnitude of the applied field. This is due to a pronounced ferroelectric effect, that is, if one plots a periodic applied field against the polarization, a hysteresis loop results. Saturation occurs at about 30 kilovolts per centimeter. Mason^{8,9} explains these phenomenae as due to the growing of favorably oriented domains at the expense of the unfavorably oriented ones. To make the analogy with ferromagnetism even more complete, Matthias¹⁰, Brettville¹¹, and Newton¹² have observed Barkhausen jumps which result from large groups

of unit dipoles in a domain, or perhaps even entire domains having their orientations changed simultaneously.

The argument in favor of domain growth is strengthened even further by the existence of electrostriction as observed by Roberts¹³, Cherry¹⁴ and Mason^{8,9}. The following mechanism has been proposed by Mason in order to explain this:

As the polarization under an applied field is increased, the growth of the favorably oriented domains must mean that large numbers of unit cells become longer in the direction of the applied field and shorter in the directions perpendicular to the applied field, giving corresponding changes in the dimensions of the gross material. Mason states that the expansion is larger than can be obtained in the analogous magnetostriction effect. Several modes of mechanical resonance have been excited in ceramic specimens by the above authors. Mechanical resonance can be observed for example by measuring K'' of a parallel plate condenser as a function of frequency. Sharp peaks are observed at frequencies corresponding to mechanical resonance frequencies. Roberts¹³ found that the entire spectrum was shifted to higher frequencies if the edges of the condenser were chipped off giving obviously higher mechanical resonance frequencies. He found further that these resonances occurred only if a strong D. C. biasing field were applied, and more important yet ^{that} mechanical resonances were never excited at temperatures above ^{the} transition point.

III.

EXPERIMENTAL WORK

The experimental work was done largely in the Collins cryostat of the low temperature laboratory of The Rice Institute. The ceramic specimens of barium titanate and barium titanate diluted with 15% and 30% strontium titanate were kindly supplied by the Bell Telephone laboratories. They were in the form of parallel plate condensers consisting of ceramic disks about 1 inch in diameter and 1.6 mm. thick on the average. The electrodes were silver and were applied by burning on silver paste. The leads were soldered directly onto the electrodes. Four specimens of pure barium titanate were sent from the Bell Telephone laboratories with electrodes and leads already attached; the diluted specimens came without electrodes so were prepared in this laboratory.

Edge effects were neglected in all measurements for two reasons; first the large value of K' ~~which~~ reduces edge effects, and second the electrodes were quite irregular in shape, making the estimation of area alone very difficult. The dimensions of the specimens are given in the appendix.

A. Low Temperature Run Number 1

Measurements made on this run were made with a Boonton 160-A Q-meter. In the Q-meter a calibrated radio frequency oscillator (Figure 1a) applies a regulated 0.02 volts R.M.S.

FIGURE 1

a. Block Diagram of The Boonton 160-A Q-Meter

b. Series Resonant Circuit

c. Series Substitution Circuit

across the 0.04 ohm non-inductive resistance which excites the series resonant circuit composed of the calibrated tuning condenser C_s and impedances connected to the external terminals 1 and 2, and 3 and 4. Thus if a calibrated inductance is connected to the external terminals 1 and 2 and C_s is varied to give series resonance as indicated by a maximum voltage on the high impedance input vacuum tube voltmeter, then the following well known relation is satisfied:

$$(12).... \quad f^2 = \frac{1}{4\pi^2 L C'}$$

where f is the frequency in cycles per second, L the inductance in henries, and C' the capacitance in farads (Figure 1b). If an unknown capacitance C is now connected across the external terminals 3 and 4, resonance can be again obtained by retuning C_s . We have

$$C' = C_1 + C$$

where C_1 and C_2 are the two respective values of C_s for resonance with C out of the circuit and in the circuit. C is given by the difference of C_1 and C_2 and is independent of the frequency and L .

The "Q" of the series resonant circuit (Figure 1b) may be defined as the ratio of the R.M.S. voltage across C' or L to the R.M.S. voltage inserted in the circuit (in this case the inserted voltage is 0.02 volts). The vacuum tube voltmeter is calibrated directly in "Q". Furthermore, if the 0.04 ohm resistance is regarded as a generator of ~~the~~ negligibly low impedance (which we can do since the 0.04 ohms is very much less than the resistance R in the resonant circuit), the circulating current I in the resonant circuit is given by the ratio of the inserted voltage to the effective series resistance R of the total circuit (Figure 1b). I is also given by the ratio of voltage across L or C' to the reactance of L or C' . Hence we write,

$$I = \frac{0.02}{R} = \frac{V}{\omega L} = \frac{V}{1/\omega C'}$$

$$\text{and } Q = \frac{V}{0.02} = \frac{C'}{\omega R}$$

In the above expressions $\omega = 2\pi f$, and V is the R.M.S. voltage read on the vacuum tube voltmeter (Figure 1a); R is so small in most circuits that V is essentially the same as the R.M.S. voltage across L . In the work described below no effort was made to calculate the loss terms $\tan \delta$

or K'' from the "Q" readings. "Q" readings obtained would ~~merely~~ indicate roughly a high loss or a low loss in the test condenser.

In the first low temperature run, a pure barium titanate specimen (designated as specimen B) was installed in the experimental chamber of the cryostat. Its leads were brought outside in a piece of commercial coaxial cable about 180 cm long. Temperatures were measured by means of a copper-constantan thermocouple, a hydrogen vapor pressure thermometer, and a helium constant volume thermometer.

The Q-meter circuit shown in Figure 1a was used except that the capacitance of the specimen was so high (about 3000 ~~mf.~~ at room temperature) that the substitution method described earlier would not work. Therefore the specimen (specimen B) was left permanently connected to terminals 3 and 4 and resonance obtained by changing the frequency.

Equation (12) would give us

$$C' = C_s + C_c + C \quad \text{where } C_s \text{ is the capacitance}$$

of the tuning condenser in the Q-meter, C_s the shunting capacitance of the coaxial cable (as measured by the substitution method described above), and C the capacitance of the specimen.

In the electrical measurements on specimen B, L was 2.5 mh. which required at room temperature a frequency of about 50 kilocycles per second, and C_c was 117 ~~mf~~ f. As the temperature was reduced, the K' of the specimen decreased, lowering the capacitance C and hence increasing the resonant frequency at low temperatures to the neighborhood of 150 kilocycles per second. Low frequencies were necessary in order to make the inductive reactance of the coaxial cable small in comparison to the capacitive reactance of the specimen; otherwise the apparent capacitive reactance would be lower than the true value. This is to be expected since the inductive reactance can be regarded to a first approximation as being in series with the specimen, and as the frequency increases the inductive reactance increases, while the capacitive reactance decreases. One other factor is ignored, -namely, the effect of the losses in the coaxial cable and specimen on the apparent K' obtained. As will be seen later, this is extremely small.

Measurements were made while cooling from 253°K down to 14.9°K . K' is seen to decrease smoothly from a value of 950 at 253°K down to 111 at 14.9°K . The values of K' obtained are given in Table 1 and are plotted versus temperature in Plates I and VII.

B. Low Temperature Run Number 2

This run was made on specimen B and a new specimen (designated by A). The experimental procedure for specimen A was identical with the above. C_c had a value of 120 ~~μ~~ f in this case. Measurements were made while cooling from 300°K down to 2.48°K. The temperatures below the normal boiling point of He (4.2K) were produced by pumping on liquid helium in the bottom of the experimental chamber. In each case the temperature was assumed to be the boiling point corresponding to the reduced pressure as measured by an open tube leading into the experimental chamber. The temperatures indicated were probably not the true temperatures of the specimen since it is not at all certain if the specimen was actually in the liquid bath, but these temperatures are given as such in interest of obtaining more accurate values of the temperature slope of K' .

For specimen A, K' was about 1200 at 293°K, decreasing to 95.9 at 2.39°K. The values obtained were in satisfactory agreement with those obtained for specimen B in the first run. Two very interesting features were observed in this run that were not noticed on the earlier run: First, the appearance of a definite peak in K' at about 274°K; the second, ~~was~~ a very broad minimum in the "Q" of the circuit at

about 50°K. This minimum would correspond roughly to a similar maximum in $\tan \delta$ or K'' . The values of K' and K'' obtained on this run for specimen A are given in Table 2, and K' is plotted versus temperature in Plates I and VII. The slope of the K' versus temperature curve was about 0.01 per °K in the 4°K region.

The measurements on specimen B were made at 500 kilocycles per second using a General Radio Type 916-A impedance bridge. The method of calculating K' , $\tan \delta$, and K'' from the impedance will be considered in the account of the next run and in the appendix. The values of the complex dielectric constant gotten for specimen B on this run did not agree with other measurements. The source of this discrepancy probably lay in errors in the calculations rather than in lack of reproducibility in the dielectric properties of the specimen, though the assumed errors were never found. These measurements show a definite maximum in K' at about 275°K and a broad maximum in $\tan \delta$ at about 75°K which correspond to similar phenomena seen in specimen A on the same run, and it was these two points of interest that inspired much of the following investigation. A few values of K' , $\tan \delta$, and K'' are given in Table 3.

C. Low Temperature Run Number 3

The next low temperature run was made on a third specimen of barium titanate (designated as specimen C). The experimental arrangement was similar to that of previous runs; the impedance measurements being made with the impedance bridge at 500, 750, 1000, and 2000 kilocycles per second. Data were taken while cooling from 298°K down to 2.83°K .

The higher frequencies employed on this run made it necessary to correct for the complete impedance of the coaxial cable rather than for the shunting capacitance alone, as was done for previous runs at lower frequencies. The bridge measured the impedance of the specimen and its leads ($z = r - ix$) such that a suitable correction for the coaxial cable would yield the impedance of the specimen, $Z = R - iX$. An account of the corrections made on this and all following runs is given in the appendix.

After the impedance of the specimen is determined, the calculation of the complex dielectric constant is made as follows. The equivalent circuit Figure 2b is employed; the parallel capacitive reactance X gives K' , while the parallel resistance R gives K'' . From elementary A.C. circuit theory we can write

$$(13) \dots \quad X_{//} = \frac{R^2 + X^2}{X} ,$$

$$\text{and } (14) \dots \quad R_{//} = \frac{R^2 + X^2}{R} ,$$

From the capacitive reactance $X_{//} = 1/\omega C$, from equation (13) and from the familiar parallel plate condenser formula

$$C = \frac{\epsilon_0 K' A}{d} , \text{ where } d \text{ is the distance between the electrodes and } A \text{ the area of each of the plates,}$$

we get

$$(15) \dots \quad K' = \frac{d}{\epsilon_0 A} \frac{X}{\omega (X^2 + R^2)} .$$

From the expression $K'' = \frac{\sigma}{\omega \epsilon_0}$, derived in the

introduction, from $R = d/\sigma A$ where σ is the specific A.C. conductivity, and from equation (14) we get

$$(16) \dots \quad K'' = \frac{d}{\omega \epsilon_0 R_{//} A} .$$

Finally, if we divide equation (16) by (15) and substitute (14) we obtain

$$(17) \dots \frac{K''}{K'} = \frac{R}{X} = \tan \delta ,$$

since equation (10) is just $\tan \delta = K''/K'$.

The values of K' , $\tan \delta$, and K'' are given in Table 5, and are plotted versus temperature in Plates I, II, III, and VII respectively. K' had a value of 1160 at 293°K which rose to a maximum of 1350 at 276°K, and decreased to 94.6 at 283°K. K' agreed quite well with other measurements, especially at the lower temperatures. The small discrepancies at low temperatures could easily be accounted for by uncertainty in the dimensions of the specimens. $\tan \delta$ was 4×10^{-3} at 298°K and increased with decreasing temperatures to a broad maximum of 49×10^{-3} at 80°K, decreasing finally, 10.8×10^{-3} at 2.83°K. A small peak in $\tan \delta$ was observed at about 270°K. K'' was about 4 at 298°K, and as the temperature decreased, K'' rose immediately to a sharp maximum of 17 at 270°K and again to a broad maximum of 20 at 206°K, finally decreasing to 1 at 2.83°K. The K' versus temperature slope in the 4°K region was again about 0.01 per °K. In these measurements, K' , $\tan \delta$, and K'' were frequency independent.

D. Measurements Using Short Leads

Prior to the run on specimen C, measurements were made at room temperature, and the temperatures of solid carbon dioxide and liquid nitrogen. Short leads consisting of two pieces of number 14 copper wire 10 inches long were used. The upper end of the leads were fastened to a textolite block for support; the lower end on which the specimens were connected was placed in a small dewar flask which contained the refrigerant for the lower two temperatures. Measurements were made with the impedance bridge for the same frequencies employed in the specimen C run described above.

Corrections for the leads were made according to the simple equivalent circuit given in Figure 2a. It is assumed that the leads are in effect a small inductance L in series with the specimen which has the impedance $Z = R - iX$, and Z is in turn shunted by the very small capacitance of the leads, C_c . L is measured by shorting out the leads at the specimen, and C_c is measured by removing the specimen and leaving the specimen terminals open. In the latter case the resulting capacitive reactance was too high to measure with the bridge, being larger than 5000 ohms at 1 megacycle per second; thus the shunting capacitance C_c is quite negligible. L was measured as approximately $0.25 \mu\text{h}$,

FIGURE 2

a. Circuit Used For Measurements
With Short Leads

b. Circuit Used In Discussion Of
Low Temperature Run Number 3

giving an inductive reactance of 3.1 ohms at 2 megacycles per second and 0.8 ohms at 500 kilocycles per second. The highest capacitance measured by this method was about 3000 ~~pf~~ ^f, which has a capacitive reactance of approximately 20 ohms at 2 megacycles per second, such that the largest correction necessary on the apparent reactance of the specimen was in the order of 15%.

Measurements were made on specimens A, B, and C, from 500 to 2000 kilocycles per second. The values of K' , $\tan \delta$, and K'' agreed reasonably well with the other measurements on the same specimens at the same temperatures except for an apparent frequency dependence. This took the form of an apparent increase in the above quantities for increasing frequencies. This could be easily explained at least in the case of K' as due to insufficient correction for the inductance L which would make the apparent capacitive reactance of the specimen lower than the true reactance, an effect that becomes larger with increasing frequency. The values of K' , $\tan \delta$, and K'' obtained are given in Table 4.

E. Low Temperature Run Number 4

The first diluted specimen (designated as specimen E) was investigated in the run described below; specimen E was a solid solution of 85% barium titanate plus 15% strontium titanate. During this run additional measurements were also made on specimen B. Data were taken on specimen E while cooling from 298°K down to 4.2°K ; and data were taken on both specimens while warming up to 178°K . Impedances were measured with the impedance bridge at 500 and 2000 kilocycles per second.

The experimental arrangement used on this run was quite different from that used earlier; this was done in an effort to improve the thermometry. The thermometers used were a copper-constantan thermocouple, a hydrogen vapor pressure thermometer, a helium pressure thermometer, and two carbon resistance thermometers. The thermocouple was used from room temperature down to 55°K ; the hydrogen vapor pressure thermometer from 20.2°K (the normal boiling point) down to 14°K (the solid hydrogen point); and the helium vapor pressure thermometer from 4.6°K down to 4.2°K (the normal boiling point). The carbon resistance thermometers were calibrated against the thermocouple and vapor pressure thermometers, and they were used to interpolate between the ranges of the other thermometers.

The carbon thermometers were in the form of thin films of amorphous carbon on 1/32" bakelite, and were 1/2" in diameter with one silver electrode deposited around the perimeter of the disk and the other in the center of the disk. These disks were firmly clamped in an arrangement of brass rings which served as the electrical connections to the thermometers. The electrical resistance of these disks gives a very large negative resistance versus temperature slope at low temperatures; typical resistance values of the two carbon thermometers at various temperatures are given below:

Temperature °K	Thermometer #1 Kilo-ohms	Thermometer #2 Kilo-ohms
99.0	16.84	12.32
58.8	19.20	13.93
37.5	21.37	15.37
19.1	24.74	16.01
4.2	34.01	27.75

Figure 3 shows the apparatus used in this run. The bottom or electrically grounded side of each specimen (a) is Woods metal soldered to the heavy brass base plate (b) which is 3" square by 1/2" thick. The ground return is through the ground post (c), to which the outer conductors of the coaxial cables (d) are soldered. The inner conduc-

FIGURE 3

Specimen Holder Used In
Low Temperature Run Number 4

tors of the coaxial cables are connected to the upper side of the specimens by means of short "zig-zag" shaped springs, made of 2 mil silver strip (not shown). These springs, which should be quite non-inductive, afforded a good electrical connection, and being very flexible prevented possible differential contraction from introducing dangerous strains in the specimens.

The coaxial cable was firmly clamped to the heavy brass yoke (e) for support; the outer plastic covering being first removed so as to give good thermal contact between the outer conductor and the brass yoke. This latter precaution was taken to remove the possibility of a heat leak down the heavy copper braid outer conductors of the coaxial cable from heating the top of the specimens.

The copper-constantan thermocouple (not shown) was taped to one of the vertical sides of the yoke (e); the two carbon resistance thermometers were taped to the top of the base plate; while the two vapor pressure thermometer bulbs were built into the base plate. These bulbs were formed by drilling horizontal 5/16" holes in the base plate and have a volume of approximately 1 cc. each. The filling tube for one of these bulbs can be seen coming out of the front side of the base plate; the filling tube of the other bulb comes out on the rear side.

Data on specimen B were taken while warming up from 5.3°K to 177°K . K' had a value of 102 at 5.3°K , and increased to 510 at 177°K . $\tan \delta$ was about 16 at 5.3°K , rising to a broad maximum of about 47×10^{-3} at 70°K , finally decreasing to 26×10^{-3} at 177°K . K'' was approximately 1.5 at 5.3°K , rising to about 13 at 177°K . These values are in reasonable agreement with previous measurements on specimens A, B, and C.

Specimen E, the specimen diluted with 15% strontium titanate, gave the following results while cooling. K' had a value of 1600 at 298°K , decreasing to 1420 at 280°K , remaining quite constant down to 249°K , and decreasing thereafter to 120 at 4.2°K . $\tan \delta$ was about 12×10^{-3} at 298°K , decreasing to about 9.4×10^{-3} at 280°K , remaining nearly constant to 220°K , rising to a broad maximum of 37×10^{-3} at 70°K , and finally decreasing to 11×10^{-3} at 4.2°K . K'' was about 20 at 298°K , decreasing to about 13 at 280°K , remaining practically constant to 250°K , decreasing to a minimum of 8 at 200°K , rising to about 12 at 130°K , and finally decreasing thereafter to 1.4 at 4.2°K . It is seen from the above that the dilution with strontium titanate had the effect of shifting the normal K' versus temperature curve towards lower temperatures as discussed in Section II, which would make all of the values of K' measured in this run higher than were obtained for pure barium titanate.

The warming up values of K' , $\tan \delta$, and K'' for specimen E were about the same as those obtained while cooling down, but showed marked hysteresis. This hysteresis in K' might be explained as due to the lack of temperature equilibrium, but in the case of K'' and $\tan \delta$ this is not true (Plates IV, V, VI, and VIII). Lack of temperature equilibrium would have shifted the broad maximums in K'' and $\tan \delta$ to the right as happened for K' , but this was not the case, so this hysteresis is more than just a lack of temperature equilibrium.

The accuracy of the measurements of the loss terms $\tan \delta$ and K'' of both specimens was impaired by the discovery after the run that the coaxial cables used on both specimens had become "lossy". The open circuit impedance of each of the cables had an effective series resistance of several ohms at 500 kilocycles per second instead of the normal several tenths of an ohm as measured before the cables were installed. Since such large resistances were measured only for the open circuited coaxial cables, one can see from Figure 4b that it is effectively R_3 that has become large, such that only at low temperatures would one expect errors resulting from the ignoring of R_3 to be appreciable. This is because the capacitive reactance X of a specimen becomes comparable to X_3 only at low temperatures where K' is low. If R_3 were large, and were neglected, one would

get apparent values of $\tan \delta$ and K'' that would be too large; K' would be unaffected since all resistances measured in the course of these measurements have a quite negligible effect on the value of K' as calculated from equation (15).

R_3 in Figure 4b represents dielectric losses in the coaxial cable; the origin of these losses is probably in damage done to the dielectric material caused by the heat necessary to assemble the apparatus. The exact location of bad spots in the coax is important because if these spots are near the specimen holder, the resulting losses might show strong temperature dependence and could not be allowed for in the calculation of the complex dielectric constant. On the other hand, if the bad spots were definitely at the top of the cryostat, they would be constant and could be allowed for in the manner outlined in the appendix. An effort was made to locate the positions of the bad places by making open circuit impedance measurements on various sections of the cables, but no conclusions were reached in this matter; consequently the equivalent circuit shown in Figure 4c was assumed, which ignored all losses in the cable.

The values of K' , $\tan \delta$, and K'' obtained for specimen B are plotted against temperature in Plates I, II, III, and VII, and are listed in Table 6. Similarly, K' , $\tan \delta$, and K'' obtained for specimen E are shown in Plates IV, V,

VI, and VIII, and in Table 7. The K' versus temperature slopes of both specimens have values of about 0.01 per $^{\circ}\text{K}$ in the 4°K region. The part played by the bad coaxial cable, if any, on the apparent hysteresis in specimen E is not known.

F. Low Temperature Run Number 5

A single specimen (designated as specimen F) was measured in this run. It was a diluted specimen composed of 70% barium titanate plus 30% strontium titanate. Measurements of K' and " Q " were made at 500 kilocycles per second with the Q-meter while cooling from 295°K down to 159°K ; and measurements of K' , $\tan \delta$, and K'' were made at 1500 kilocycles per second with the impedance bridge while cooling from 134°K down to about 14°K .

The coaxial cable used was made out of two concentric pieces of copper tubing. The inner conductor was of $1/8$ " copper tubing; the outer conductor, of thin walled $1 1/8$ " copper tubing. Polystyrene spacers were used to support the inner conductor. Temperatures were measured with a copper-constantan thermocouple for temperatures above 55°K and with the helium constant volume thermometer used on earlier runs for temperature below 55°K .

The Q-meter measurements were made by the series substitution method (Figure 1c). In the series substitution method the unknown condenser C is connected in series with the external inductance L . Resonance is obtained by varying the calibrated tuning condenser C_s . If we call the value of C_s at resonance C_2 and retune C_s with the unknown condenser C shorted out, calling this new value of C_s , C_1 , we can easily show that

$$C_1 = \frac{C C_2}{C + C_2} \quad \text{or} \quad C = \frac{C_1 C_2}{C_2 - C_1}.$$

In this run the upper end of the coaxial cable was connected in series with L , such that the above formula gives an apparent capacity C^* , from which the capacitive reactance of the specimen and its leads was calculated. Corrections for the coaxial cable were made in the manner outlined in the appendix.

K' is plotted versus temperature in Plates IV and VIII. At room temperature K' was about 3600; and as the temperature decreased, K' rose to a high maximum of 6000 at 274°K, decreasing rapidly to 2500 at about 250°K, then after falling off more slowly, reaching a value of 200 at 14°K. Both the

value of the extremely large maximum and its temperature was to be expected from the results reported by Jackson and Reddish⁴, Roberts¹³, and others.

For the bridge measurements alone K'' decreased smoothly to about 9 at 14°K. $\tan \delta$ was about 16 at 14°K and appeared to have a maximum of about 38 near 120°K. Although data were not taken at high enough temperatures with the bridge to get the true shape of this curve, the "Q" values measured at higher temperatures with the Q-meter decreased as the temperature decreased, which would seem to support the existence of a hump in $\tan \delta$ since "Q" values vary inversely with electrical losses in the specimen.

K'' , $\tan \delta$, and $1/Q$ are plotted versus temperature in Plates V, and VI; K' , $\tan \delta$, K'' , and "Q" are listed in Table 8. The slope of the K' versus temperature curve for specimen F is still high at 14°K, giving no indication that it might become less than 0.01 in the 4°K region.

K' vs.

- x Specimens
- o Specimens
- Δ Specimens
- $\square$ Specimens

Plate I

K' vs. Temperature

specimen C, run #3
 specimen A, run #2
 specimen B, run #1
 specimen B, run #4

Plate II tan δ vs Temperature

x Spec. C, run #3
o Spec. B, run #4

tan $\delta \times 10^3$

T $^{\circ}$ K

Plate III

K'' vs. Temperature

x Specimen C, run #3

o Specimen B, run #4

Plate IV

$K' \times 10^{-3}$
 vs. Temperature
 x Specimen E, run #4
 o Specimen F, run #5

Plate V

$\tan \delta$ and $1/Q$ vs. Temperature

x Specimen E, run #4, $\tan \delta$
 o Specimen E, run #5, $\tan \delta$
 Δ " " " " $1/Q$

$\tan \delta \times 10^3$

50

40

30

20

10

0

0

50

100

150

200

250

300

$T^\circ K$

$1/Q \times 10^3$

9

8

7

6

Plate VI

K" vs. Temperature

x Specimen E, run #4

o Specimen F, run #5

K"

20

15

10

5

0

50

100

150

200

250

300

T °F

Plate VII

K' vs. Temperature

x Specimen B, run #1

o Specimen B, run #4

Δ Specimen A, run #2

□ Specimen C, run #3

K'

150

140

130

120

110

100

90

0

10

20

30

40

$T \cdot K$

Plate VIII

K' vs. Temperature

x Specimen F, run #4

o Specimen F, run #5

K'

250

200

150

100

50

0

10

20

30

$T^{\circ}K$ 40

IV. DISCUSSION OF RESULTS

The real part K' of the complex dielectric constant $K = K' - ik''$ of pure barium titanate ceramic has been investigated from room temperature down to 2.38°K . The values obtained for three different specimens (designated as A, B, and C) are plotted against temperature in Plates I and VII. Plate I shows the commonly accepted value of about 1150 at 300°K . The maximum at 275°K corresponds to a similar *peak* observed for static measurements by von Hippel², and in some cases occurs for periodic fields, but in the curve shown here it is considerably more pronounced than has been observed previously at any frequency. Below 275°K , K' falls off with decreasing temperatures to about 100 in the 4°K region. There appeared to be no frequency dependence within experimental error. The differences existing between values for the different runs can easily be explained as due to errors in *the* measurement of the dimensions of the specimen, because the areas of the electrodes are difficult to determine accurately.

The values of $\tan \delta$ are plotted versus temperature in Plate II. The large hump in $\tan \delta$ at low temperatures observed on all specimens, pure and dilute, has not been observed previously. The general rise of $\tan \delta$, as the temperature decreases, does not agree with measurements reported by von Hippel², who gave $\tan \delta$ steadily decreasing with lowering

temperatures. Von Hippel also found a large peak in $\tan \delta$ near 275°K which corresponds to the small peak observed in the curve for specimen C at the same temperature.

The imaginary part K'' of the dielectric constant for pure barium titanate is shown on Plate III. The values near room temperature are in agreement with those given by von Hippel² and Roberts¹³, but the increase below room temperature was not found by Roberts, who worked at 400 kilocycles per second, a frequency that is not far different from the frequencies employed in the course of this investigation.

All measurements of K' , K'' , and $\tan \delta$ reported here seem to be frequency independent; any apparent small dependency on frequency could be easily explained on the basis of incomplete corrections for the impedance of the coaxial cables used. Von Hippel observed a slight decrease in K' and $\tan \delta$ for ceramic barium titanate with increasing frequencies in the frequency range employed here, so that we agree on these matters.

Mason⁹ and Merz¹⁵ have made measurements on single domain crystals. Both report an extremely high K' of 10,000 or more along the a axis of the crystal and several hundred along the c axis, but they differ on the matter of frequency dependence. Mason reports a definite decrease of some 15% in K' from 500 to 2000 kilocycles per second; on the other

hand Merz found no noticeable change in K' along either axis up to 40 megacycles per second. No measurements were made on K'' or $\tan \delta$ for the single domain crystals. The exact relation existing between single domain crystal values of K' and values for the much more complicated ceramic material is not as yet clear.

The effects of the dilution of barium titanate with 15 and 30% strontium titanate are shown in Plates IV, V, VI, and VIII. The dilution seems to have shifted the normal barium titanate K' curve to lower temperatures. In the case of 15% strontium titanate dilution (specimen E) the large peak normally occurring at 393°K has apparently been shifted to a point just above room temperature since all values of K' are somewhat higher than for the pure specimen (1600 at 298°K and 120 at 4.2°K). The 30% dilution (specimen F) has its large peak of 6000 at 275°K , giving a value of 200 at 14°K , representing even a further shift. This shift in the large peak in K' is in agreement with the measurements reported by Jackson and Reddish⁴.

As mentioned earlier in section II, the high dielectric constant of the alkaline earth titanates is due to loose binding of the titanium ion in the unit crystalline cell. Barium titanate, which has a much higher K' than the other alkaline earth titanates, undergoes a transition at 393°K from the cubic

form to the tetragonal form.

Unit Cell of Barium Titanate

○ Ba ion; ⊖ O ion; ⊘ Ti ion

In the tetragonal form, which exists below 393°K , the titanium ion is shifted towards one of the oxygen atoms, giving a permanent dipole moment. Groups of these dipoles are lined up forming domains that have permanent polarization of some 30 kilovolts per centimeter. In the ceramic material many such domains are oriented at random, giving in the bulk material a resultant polarization of zero.

Mason^{8,9} explains the unusually high values of the dielectric constant of barium titanate (as compared to the other alkaline earth titanates) as due to the growth of the favorably oriented domains at the expense of the less favor-

ably oriented domains; it is difficult to see how this mechanism alone could explain the high values of the dielectric constant that exist for temperatures above the transition point (393°K). On the other hand, it was shown by Wul that there was a general increase in the dielectric constant as the size of the alkaline earth ion increased; and von Hippel² and Megaw⁶ stated that the large size of the alkaline earth ion may distort the octahedral TiO_6 group allowing the loose binding of the titanium ions, thus explaining in part, at least, the large dielectric constant of barium titanate.

The temperature dependence of K' at low temperature could be explained on the basis of an increase in the binding of the titanium ion as the temperature decreases; thus on the simple dielectric theory given earlier, the force constant

f in equation (1) ~~i~~ncreases as the temperature decreases. This simple mechanism, of course, fails to take the cooperative phenomena of the domain structure into account. Similarly, the large values of K'' found between room temperature and liquid helium temperatures could be explained by equation (1) as due to large values of the damping coefficient r , but again the true situation is much too complicated to be treated in any fruitful manner by such a crude model as expressed by equation (1).

At the outset it was mentioned that the original purpose

of this investigation was the verification of the large value of the slope of K' versus temperature in the liquid helium region for barium titanate as reported by Wul. This large value of the slope was found for three different specimens of pure barium titanate, and in addition, measurements were made on solid solutions of strontium titanate in barium titanate, in order to see what effect this dilution would have on the slope at low temperatures. The temperature coefficient of K' , $1/K' dK'/dT$ was found to be approximately 0.01 per $^{\circ}K$, just as was found for the pure barium titanate.

One interesting possibility is that barium titanate might exhibit an appreciable electro-caloric effect at low temperatures. Preliminary investigations of this are now being made in this laboratory.

V.

CONCLUSIONS

In conclusion, we may state that from an experimental standpoint the dependence of the real part of the dielectric constant, K' , on temperature shows general agreement between our work and that reported by other investigators. The theoretical interpretation presents a challenging problem, particularly with respect to the surprisingly large dependence of K' on temperature at 4°K. The experiments on diluted specimens, wherein as much as 30% of the barium ions are replaced by the smaller strontium ions, allow us to conclude that at 4°K the magnitude of K' is increased by the substitution, but the temperature dependence is unaffected. The conclusions drawn from the studies on the imaginary part of the dielectric constant, K'' , are that its frequency independence ^{does not} support a simple concept of a titanium ion dipole oscillator having a damping term proportional to the displacement velocity; ^{also} ~~but~~ the temperature dependence of K'' could not be explained by so simple a mechanism. We suggest that the concept of domain growth must be introduced into the theory of K'' . We conclude that the dilution with strontium ions in place of barium ions does very little to the temperature dependence of K'' .

VI.

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VII.

APPENDIX

A. Corrections for Coaxial Cable Impedance

In order to measure the complex dielectric constant of a specimen, it was necessary to measure its impedance as seen "through" a coaxial cable. The impedance of the specimen is $Z = R - X$, where R is the effective series resistance and X the effective series capacitive reactance. The measuring instrument at the other end of the coaxial cable does not measure the true impedance of the specimen but, instead, measures an apparent impedance $z = r - ix$, which is the true impedance Z altered somewhat by the impedance of the coaxial cable. The problem then is one of correcting the apparent impedance z to get the true impedance Z .

By well known principles of A.C. circuit theory, we may consider the coaxial cable as a three terminal network in which both ends of one of the conductors is regarded as a single terminal, the two ends of the other conductor being the other ~~two~~ terminals. Then by making suitable measurements on the cable, we can find an equivalent "T" section that is indistinguishable from the coaxial cable with the one qualification that the impedances of the equivalent "T" section may vary with frequency.

Figure 4a shows the specimen represented as the impedance $R - iX$ and the coaxial cable represented by the equivalent "T" section, composed of Z_1 , Z_2 , and Z_3 . If these impedances are known at a given frequency, then the calculation of R and X from the measured values of r and x can be readily made.

From elementary circuit theory we can easily see that the components of the "T" section can be calculated from the following measurements on the "T" section (and hence on the actual coaxial cable): With the specimen removed (Figure 4a) the impedance Z_{o1} across terminals 1 and 2 with terminals 3 and 4 shorted is measured; and in a similar manner one measures Z_{o2} and Z_{s2} from the specimen end of the cable. From any three of these four impedances we can calculate the three components of the "T" section.

The coaxial cables used in the course of the experiment were assumed to be electrically symmetrical and constant at all temperatures so that $Z_{o1} = Z_{o2}$ and $Z_{s1} = Z_{s2}$; hence $Z_1 = Z_2$. We find then that

$$Z_3 = \sqrt{Z_{o1}(Z_{o1} - Z_{s1})}, \text{ and } Z_1 = Z_2 = Z_{o1} - \sqrt{Z_{o1}(Z_{o1} - Z_{s1})}.$$

The resulting equivalent circuits are of the form shown

* See page iv for erratum

FIGURE 4

a. Equivalent T Section Used In Discussion
Of Coaxial Cable Corrections

b. Equivalent T Section Used In Discussion
Of Coaxial Cable Corrections

c. Simple T Circuit Used In Discussion
Of Coaxial Cable Corrections

in Figure 4b; namely, equal resistances and equal inductances in the two horizontal arms of the "T" section, and a series resistance and capacitance in the vertical arm. The values of these impedances change with frequency, so it is necessary to determine the equivalent "T" section for each frequency employed in the course of the low temperature run.

The effective series resistance R of a specimen was in general much higher than the resistances in the equivalent circuits of the coaxial cables so that to a good approximation R_1 and R_3 (Figure 4b) could be neglected, giving the circuit shown in Figure 4c. This latter circuit is quite simple and makes calculations of the impedance of the specimen comparatively easy. On the analysis of the circuit in Figure 4c one finds that the impedance z of the specimen is given by

$$Z = r F^2 + i \left(F(X_1 + x) - X_1 \right) \quad \text{where} \quad F = \frac{X_3}{X_1 + x - X_3} .$$

The above expression was used to make the calculations for the fourth and fifth low temperature runs, but in the third run an additional correction was made. The somewhat more complicated circuit of Figure 4b was used to calculate a few selected points from room temperature down to liquid helium temperature. The impedances obtained in this way were then compared with those calculated by the expression above, and the errors introduced by ignoring the coaxial cable resistances were estimated over

the entire temperature range.

* Erratum: Line 12, page ii should read, "-2 with terminals 3 and 4 open is measured; next the impedance Z_S , across terminals 1 and 2 with terminals 3 and 4 shorted is -."

B. Measured Values of Dielectric Constant

TABLE 1
(specimen B, 1st. run)

Temperature °K	K'	Temperature °K	K'
253	950	31	144
233	875	25.5	131
232	761	23	125
199	630	20.1	121
187	565	19.5	120
163	456	19.2	120
148	414	19.0	117.5
133	364	17.9	117
116	323	16.8	115
101	285	16.4	114
80	249	16.1	114
67	228	15.8	114
55	196	15.2	112
41	159	14.9	111

TABLE 2
(specimen A, 2nd. run)

Temp. °K	K'	Q	Temp. °K	K'	Q	Temp. °K	K'	Q
293	1203	54	17.8	117	37.5	5.9	100.5	64
274	150	40	16.5	115	39	5.4	100.5	67.5
259	1500	42	15.2	113	40	4.4	99.7	69
241	1945	43	14.5	111	42	4.28	98.9	70
226	870	40	13.5	110	43	4.28	98.5	71
213	805	35	14.0	111	42	4.23	98.5	71
193	629	33	13.2	110	43	3.54	97.0	73
175	515	31	12.7	109	44	3.46	97.0	73
139	391	28	11.3	106	48	3.38	97.0	73
120	344	25	10.5	106	50	3.08	96.5	79
95	312	19	10.2	105	51	3.03	96.5	79
80	241	12	9.4	104.5	52	2.93	96.5	80
69	234	12	8.6	104	54	2.64	96.1	83
53	221	15	8.6	103	55	2.54	95.9	84
29.8	141.7	20	8.2	103	56	2.43	95.9	84
26.8	134.3	19	7.8	102.5	59	2.39	95.9	86
24.2	129.5	20	7.5	102	59	2.48	96.1	86
23	126	21	7.5	102	59			
21.4	123	27	6.2	101.4	61			
19.5	119	26	6.0	101	63			

TABLE 3

(specimen B, 2nd. run, 500kc.)

Temp. °K	K'	$\tan \delta \times 10^3$	K''
295	1237	5.95	7.4
275	1305	7.52	9.8
250	1090	12.2	13.3
200	677	19.5	13.2
150	485	27.2	13.2
100	354	31.8	11.3
75	305	32.1	9.8
50	262	31.8	8.3
40	245	28.6	7.0
30	232	25.3	5.9
25	219	23.0	5.0
20	211.5	21.1	5.0
15	206	18.4	3.8
10	197.5	14.2	2.8
7.5	195	12.3	2.4
4	194	10.5	2.0

TABLE 4
(measurements with short leads)

Specimen A				
Temperature	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
Room	500	1140	3.95	4.5
Room	1000	1160	4.46	5.2
Room	2000	1300	8.0	10.4
Solid CO ₂	500	590	23.9	14.1
Solid CO ₂	1000	595	27.1	16.1
Solid CO ₂	2000	623	34.4	21.4
Liq. N ₂	500	242	45.5	11.0
Liq. N ₂	1000	238	47.9	11.4
Liq. N ₂	2000	236	51.9	12.2
Specimen B				
Room	500	1100	3.57	3.9
Room	1000	1120	4.37	4.9
Room	2000	1280	7.14	9.1
Solid CO ₂	500	603	24.2	14.6
Solid CO ₂	1000	596	21.7	12.9
Solid CO ₂	2000	617	33.8	20.9
Liq. N ₂	500	233	45.6	10.6
Liq. N ₂	1000	230	48.5	11.1
Liq. N ₂	2000	231	53.0	12.2

Continued:

TABLE 4
Specimen C

Temperature	Frequency	K'	$\tan \delta \times 10^3$	K''
Room	500	1140	3.01	3.4
Room	1000	1180	3.77	4.5
Room	2000	1310	5.81	7.6
Solid CO ₂	500	695	24.3	16.9
Solid CO ₂	1000	713	27.0	19.3
Solid CO ₂	2000	760	32.2	24.5
Liq. N ₂	500	251	45.0	11.3
Liq. N ₂	1000	249	48.7	12.1
Liq. N ₂	2000	247	53.1	13.1

TABLE 5
(specimen C, 3rd. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
298	1000	1164	3.78	4.4
297	500	1162	3.47	4.0
295	500	1182	3.89	4.6
291	500	1227	4.91	6.0
288	500	1250	5.95	7.4
287	500	1274	7.01	8.9
284	500	1320	8.30	11.0
281	500	1350	9.44	12.7
276	500	1351	10.4	14.1
270	500	1210	13.9	16.8
267	500	1121	13.1	14.6
265	500	1087	11.9	12.9
264	500	1068	10.9	11.7
264	500	1067	10.1	10.8
263	500	1067	10.1	10.8
262	500	1050	8.38	8.8
248	500	956	15.5	14.8
243	500	930	16.6	15.4
231	1000	894	20.8	18.6
227	1000	858	21.4	18.4

CONTINUED:

TABLE 5
(specimen C, 3rd. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
213	500	800	23.5	18.8
212	500	771	25.1	19.4
206	750	716	27.6	19.8
201	750	658	28.1	18.5
193	1000	573	29.5	16.9
188	1000	551	30.4	16.8
180	500	515	29.5	15.2
175	500	496	29.4	14.6
170	750	469	31.2	14.6
167	750	457	31.8	14.5
159	1000	431	32.6	14.1
156	1000	422	32.8	13.9
150	500	406	33.6	13.7
145	500	390	35.1	13.71
135	750	359	38.7	13.9
132	750	352	39.2	13.8
125	1000	332	41.4	13.8
121	1000	325	42.0	13.7
116	500	323	41.3	13.4
111	500	315	41.6	13.1
100	750	282	45.0	12.7

Continued:

TABLE 5
(specimen C, 3rd. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
98	750	276	45.4	12.5
88	1000	247	46.5	12.0
85	1000	240	48.6	11.7
78	500	227	47.3	10.7
64	750	193	47.5	9.2
50	1000	166	46.8	7.8
39	500	150.0	43.3	6.5
33	750	136.7	42.5	5.9
27.5	1000	128	41.6	5.3
25	500	129.3	37.7	4.9
22	750	119	36.7	4.4
20	1000	114.3	35.7	4.1
19	500	114.3	32.9	3.8
18.5	750	112.1	32.1	3.6
18	1000	110.7	32.0	3.5
16.5	2000	106.0	32.0	3.5
16.5	500	113.2	33.8	3.8
23.5	750	122	38.4	4.7
21.5	1000	116.7	36.4	4.3
19.5	2000	111.8	35.0	3.6
17	500	111.6	30.4	3.4

Continued:

TABLE 5
(specimen C, 3rd. run)

Temperature	Frequency	K'	$\tan \delta \times 10^3$	K''
15.5	750	108.7	29.4	3.2
14.5	1000	106.4	28.0	3.0
13	2000	103.7	26.1	2.7
12.5	750	104.6	24.6	2.6
12	1000	102.9	24.2	2.4
10	2000	102.0	21.5	2.2
9.5	500	100.2	20.7	2.1
8.5	750	101	20.3	2.1
7.5	1000	99.6	19.6	2.0
6.0	2000	98.4	19.2	1.9
6.5	500	99.5	17.4	1.73
6.0	750	99.0	16.9	1.67
6.0	1000	97.8	17.1	1.67
6.0	2000	97.5	17.4	1.70
4.3	500	96.9	14.6	1.42
4.3	750	96.7	14.5	1.40
4.3	1000	95.9	14.7	1.41
4.3	2000	95.0	15.1	1.44
4.3	500	96.8	14.1	1.37
2.83	500	94.6	10.8	1.02

TABLE 6
(specimen B, 4th run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
5.3	2000	102.0	11.9	1.22
5.3	500	102.3	16.3	1.67
6.6	500	102.9	16.6	1.71
7.5	500	104.4	16.2	1.90
10.9	500	107.9	20.9	2.25
12.1	500	109.7	24.9	2.73
15.4	500	114.8	29.8	3.42
16.5	500	116.6	31.2	3.64
18.9	500	122.1	34.9	4.26
19.7	500	123.2	35.5	4.37
20.2	500	123.2	35.7	4.39
39.4	500	155.6	42.6	6.63
42.4	2000	165.3	51.2	8.5
43.3	500	161.4	43.2	7.0
49.2	2000	167.3	51.0	8.5
50.8	500	176.2	43.9	7.7
53.4	500	182.4	42.9	7.8
56.7	500	187.4	45.5	8.5
61.3	500	198.1	46.0	9.1
68.0	500	210	46.7	9.8
77.4	500	231	45.1	10.4
79.3	2000	227	53.5	12.1

Continued:

TABLE 6
(specimen B, 4th run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
84.2	500	248	45.0	11.1
89.5	500	258	44.0	11.4
99.3	500	278	41.6	12.8
103.8	500	288	41.3	11.9
146.4	500	395	31.6	12.5
152.3	500	396	31.2	12.4
176.7	500	510	26.3	13.4

TABLE 7
(specimen E, 4th. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
298	500	1605	12.5	20
296	500	1571	11.1	17
289	500	1560	9.5	15
281	500	1416	9.2	13
249	500	1412	9.3	13.2
236	500	1217	9.4	11.4
232	500	1110	10.2	11.3
226	500	1030	9.1	9.5
213	500	883	9.7	8.6
200	500	808	9.9	8.0
190	500	753	11.7	8.8
185	500	718	14.8	10.7
178	500	654	17.4	11.4
171	500	585	19.8	11.6
164	500	539	21.5	11.6
159	500	511	21.2	10.8
154	500	490	24.2	11.9
138	500	420	29.1	12.2
124	500	377	32.8	12.3
114	500	344	34.4	11.8
107	500	323	35.4	11.4

TABLE 7
(specimen E, 4th. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
95	500	295	36.2	10.7
81.6	500	259	36.1	9.4
71.6	500	238	35.7	8.5
58.8	500	209	36.1	7.5
37.5	500	174.2	31.8	5.5
22.0	500	145.6	24.8	3.6
19.1	500	140.1	23.3	3.3
16.7	500	138.2	21.55	3.0
15.8	500	135.8	20.9	2.8
15.6	500	135.8	20.9	2.8
15.1	500	134.6	20.7	2.8
14.7	500	134.3	20.4	2.7
13.9	500	133.1	19.7	2.6
12.6	500	131.0	18.9	2.5
12.0	500	129.6	17.9	2.3
11.0	500	128.6	16.9	2.1
10.7	500	128.6	19.2	2.5
9.7	500	126.8	19.0	2.4
8.7	500	125.3	16.0	2.0
7.0	500	124.3	15.0	1.86
6.0	500	123.7	13.9	1.72

Continued:

TABLE 7
(specimen E, 4th run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
5.4	500	122.2	13.1	1.60
5.3	500	121.7	12.5	1.52
5.3	500	121.7	12.7	1.55
5.3	2000	120.2	13.3	1.6
5.3	500	121.6	12.6	1.53
4.2	500	120.0	11.6	1.39
4.5	500	121.0	12.8	1.55
5.4	500	122.0	12.6	1.54
6.0	500	122.4	12.9	1.59
6.2	500	124.2	15.0	1.87
9.5	500	126.8	15.2	1.52
13.0	500	131.0	19.1	2.5
14.2	500	132.4	20.2	2.7
17.4	500	137.6	21.9	3.0
18.3	500	139.1	22.7	3.2
23.0	500	145.9	20.7	3.0
25.2	500	149.9	21.0	3.2
40.4	500	172.6	31.1	5.4
41.4	2000	169.6	34.7	5.9
44.3	500	183.9	32.6	6.0
46.8	500	183.9	32.8	6.0

Continued:

TABLE 7
(specimen E, 4th run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
47.9	2000	178.3	39.5	7.0
52.8	500	192.4	33.7	6.5
57.2	500	199.5	30.1	6.0
60.5	500	206	34.5	7.1
68.3	500	221	34.9	7.7
77.6	500	231	34.3	7.9
77.7	2000	239	39.9	9.5
84.9	500	260	35	9.1
89.2	500	269	34.8	9.4
99.4	500	293	33.5	9.8
103.7	500	302	33.0	9.9
146.6	500	424	20.9	8.9
152.3	500	449	18.9	8.5
178.0	500	574	14.6	8.4

TABLE 8
(specimen F, 5th. run)

Temperature °K	Frequency kc.	K'	$1/Q \times 10^3$
295	500	3610	5.99
292	500	3810	
290	500	4140	
288	500	4450	6.25
286	500	4700	
284	500	4950	
282	500	5330	
280	500	5610	
276	500	5840	
274	500	6040	6.21
273	500	5920	
271	500	5840	
269	500	5720	
266	500	5690	
265	500	4880	6.25
263	500	4610	6.33
261	500	4230	6.33
258	500	3710	
256	500	3470	6.41
253	500	3230	
253	500	2630	

Continued:

TABLE 8
(specimen F, 5th. run)

Temperature °K	Frequency kc.	K'	1/Q x10 ³
251	500	2770	
244	500	2530	6.45
237	500	2340	
229	500	2270	6.50
211	500	2030	6.56
207	500	1920	6.67
204	500	1827	6.71
201	500	1735	6.75
198	500	1610	6.85
196	500	1531	6.92
193	500	1475	7.00
191	500	1500	7.05
187	500	1444	7.15
183	500	1376	7.25
179	500	1288	7.35
175	500	1225	7.46
171	500	1214	7.63
167	500	1128	7.67
159	500	1000	8.40

Continued:

TABLE 8
(specimen F, 5th. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
134	1500	760	33.3	25.3
125	1500	690	30.1	26.3
115	1500	618	38.1	23.5
106	1500	550	37.9	21
93	1500	480	36.7	17.9
82	1500	434	35.7	15.5
75	1500	401	33.6	13.5
69	1500	367	34.0	12.5
63	1500	345	33.7	11.6
56	1500	322	33.0	10.6
49	1500	303	32.5	9.9
44	1500	289	31.6	9.1
40	1500	277	30.8	8.5
36	1500	280	31.0	8.7
33	1500	256	28.9	7.4
29	1500	247	28.0	6.9
26	1500	234	25.1	5.9
22	1500	226	23.5	5.3
19.5	1500	216	21.0	4.5
16	1500	209	18.6	3.9
14	1500	203.5	17.7	3.6

Continued:

TABLE 8
(specimen F, 5th. run)

Temperature °K	Frequency kc.	K'	$\tan \delta \times 10^3$	K''
15	1500	209	19.2	4.0
15	1500	212	20.1	4.3
20.5	1500	223	23.4	5.2
22	1500	227	23.0	5.4