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INTERFACIAL POLARIZATION IN NaCl EXAMINED IN SUPERIMPOSED a.c. AND d.c. VOLTAGE

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The presented paper gives the results of experimental measurements of the capacitance and the loss factor of a simple multilayer dielectric system, and of the variation of these properties with temperature, when the system is subjected to superimposed d.c. and a.c. fields. A simple theoretical model is proposed to explain the results. The system consists of a single crystal of NaCl between platinum electrodes. The multilayer nature of the system arises from the imperfect contact between the crystal and the electrodes. It is supposed that the platinum-crystal interface is equivalent to a thin dielectric layer. It was found that the bias d.c. voltage causes a decrease in capacitance and a decrease or increase in tan δ measured by an a.c. field. These changes are predicted by the theoretical model, the decrease or increase in tan δ occurring according to whether the phase angle of the polarization current is greater or less than the phase angle of the sum of the conductive and capacitative current.

ИССЛЕДОВАНИЕ МЕЖДУСЛОЙНОЙ ПОЛЯРИЗАЦИИ В NaCl С ПОМОЩЮ НАЛОЖЕННОГО ПЕРЕМЕННОГО И ПОСТОЯННОГО НАПРЯЖЕНИЯ

В работе приводятся результаты измерений емкости и коэффициента потер в простой многослойной диэлектрической системе в случаях когда эта система подвергнута действию наложенных переменных и постоянных полей. Предлагается простая теоретическая модель для обяснения этих результатов. Система составлена из кристалла NaCl расположенного между платиновыми электродами. Многослойный характер системы вытекает из несовершенства контакта между кристаллом и электродами. Предполагается, что поверхность раздела платина-кристалл эквивалентна тонкому диэлектрическому слою. Было обнаруженно, что приложенное постоянное напряжение способствует уменшению емкости и уменшению или повышению танг. δ измеряеммых с помощю переменного поля. Эти изменения предсказанны в теоретической модели – постоянное напряжение понижает поляризационный ток и вследствие того происходит уменшение или повышение танг. δ в зависимости от отношения фазового угла поляризационного тока и фазового угла тока представленного суммой проводящего и емкостного токов.

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I. INTRODUCTION

In practice dielectrics are frequently subjected to superimposed a.c. and d.c. fields [1]. Measurements of safe load and life time of capacitors stressed by combined d.c. and a.c. voltages have shown that for some dielectrics the d.c. voltage often causes a decrease in tan δ compared with its value when measured with an a.c. voltage only, [2—6]. This result shows that the energy losses from a.c. and d.c. voltages cannot be simply added. The decrease in tan δ that occurs after superimposing a d.c. voltage can be explained by the presence of interfacial polarization arising from a limited migration of carriers. It is suggested that the d.c. voltage binds part of the free carriers and thereby decreases the number of ions available as carriers in the alternating current.

Previous investigations of the influence of superimposed voltages have been concerned with capacitors with multilayer dielectrics. In the present work we have chosen, for detailed analysis, a material whose structure is well established, and whose carriers and their concentration, mobility and activation energy are all known. NaCl is a particularly suitable material. Its ionic conductivity is caused by Na ions only [7]. It is known that the mobility of ions in NaCl is caused by the existence of Schottky defects, i.e. by a vacancy mechanism. The influence of the concentration of charge carriers on charge transport phenomena can be studied by doping with bivalent cation admixtures, which introduce into the crystal an equal number of cations and vacancies. Information about polarization processes can be deduced from the temperature dependence of tan δ. In addition to a low temperature peak in tan δ caused by dipoles formed by vacancies and admixtured cations, there is also a high temperature peak caused by interfacial polarization [8, 9, 11]. The temperature at which this peak occurs depends on the quantity of admixture [12] and the height of the peak depends on the quality of contact of the sample with the electrode [13]. When the sample of NaCl is not coated with graphite or other conducting material it forms a system with an interlayer of low conductivity between the sample and the Pt electrodes. This is the simplest case of the occurrence of interfacial polarization. Investigation of this type of multilayer system rather than one consisting of layers of different dielectrics is not complicated by the diffusion of different material particles across interfaces.

The aim of this work is to investigate the influence of the superimposition of d.c. and a.c. fields on interfacial polarization and to give the explanation of the mechanism of the action of a combined field on dielectric characteristics of the model dielectric.

It is hoped that the model suggested in this paper could be used as a basis also for predicting the behaviour of combined systems of dielectrics in which interfacial polarization occurs and for predicting the maximum admissible values of combined voltages across these systems.

It is important to remember that interfaces cannot be avoided in any arrangement of dielectrics, and indeed these are often useful for increasing the capacitance. Suppression of interface resistance by graphite coating [13] increases the total conductivity of the system and significantly increases tan δ and although it decreases the peak in tan δ arising from interfacial polarization it causes a general rise in tan δ and this makes it less suitable as a practical dielectric.

The measurements in our experiments show that superimposition of a d.c. voltage can decrease or increase the value of tan δ compared with the value measured with only alternating voltage. A theoretical explanation is given of this behaviour of tan δ and of the decrease in capacitance. The changes in tan δ and capacitance are all consequences of the changes in polarization current caused by the superimposition of a d.c. field. The influence of superimposed d.c. field on elastic polarizations is not discussed since at acoustical frequencies the effect on tan δ would be negligible. The influence of superimposed fields on dipole polarization is discussed in our paper [14].

II. EXPERIMENTAL PART

The capacitance, conductance and tan δ of the samples were measured on a General Radio capacitance bridge, type 1615 A. A d.c. voltage up to 200 V from a battery was superimposed on an alternating voltage of 10 V rms, 0.5—50 kHz.

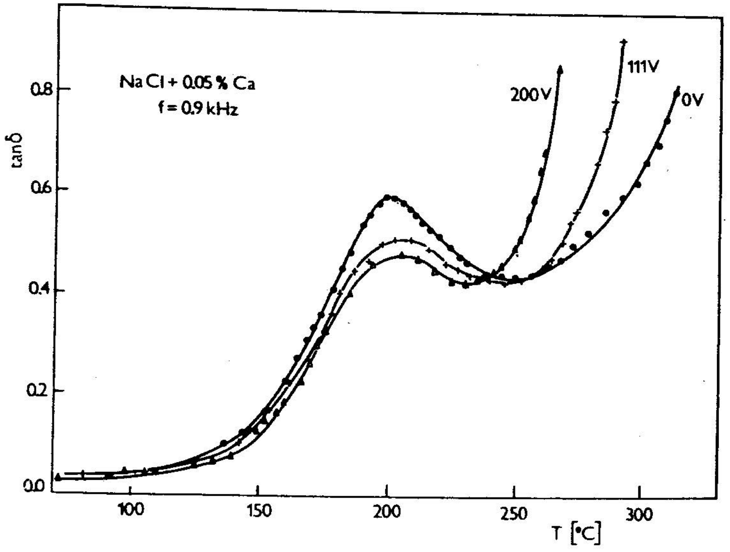

Fig. 1. Temperature dependence of tan δ by $E_{=} = 1$ V/mm without and with superimposed d.c. voltage.

The sample was laid between platinum electrodes held by springs which ensured that approximately equal pressures were exerted on both sample-electrode contacts. The samples were sliced out of a single crystal NaCl and had a surface area of 1 cm^2 and a thickness of 1 mm. After slicing the samples were not polished or coated. Between measurements the electrodes were shortcircuited. Heating and cooling was at the rate 1.5 °C/min.

Measurements were made on samples of NaCl containing 0.05 mol % $CaCl_2$.

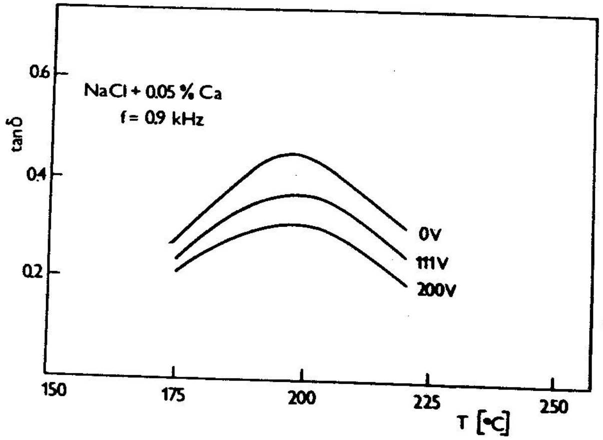

Fig. 2. Relative heights of peaks derived from simplified interpolation of conductive components of tan δ.

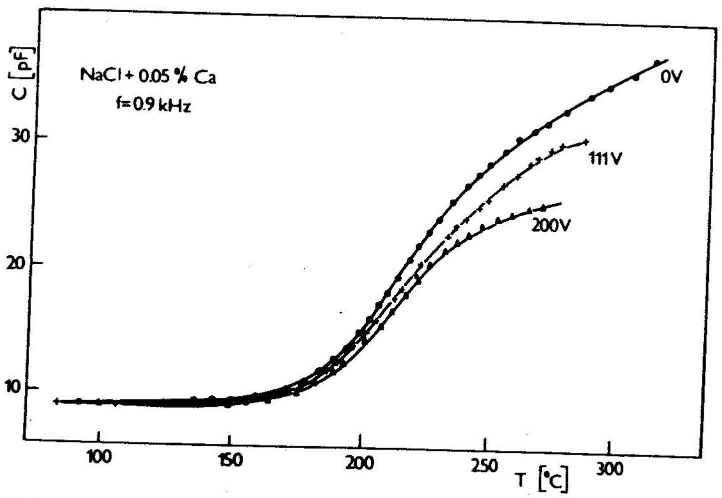

Fig. 3. Temperature dependence of capacity without and with superimposed d.c. voltage.

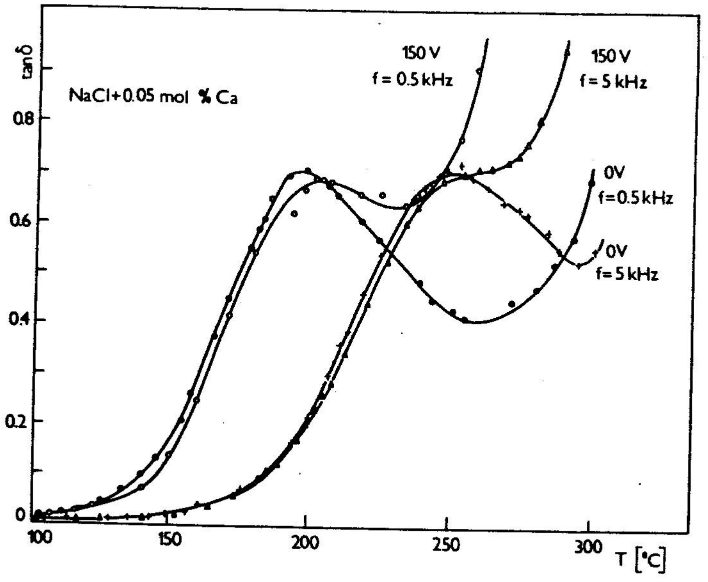

Fig. 4. Temperature dependence of tan δ at marked frequencies without and with superimposed d.c. voltage.

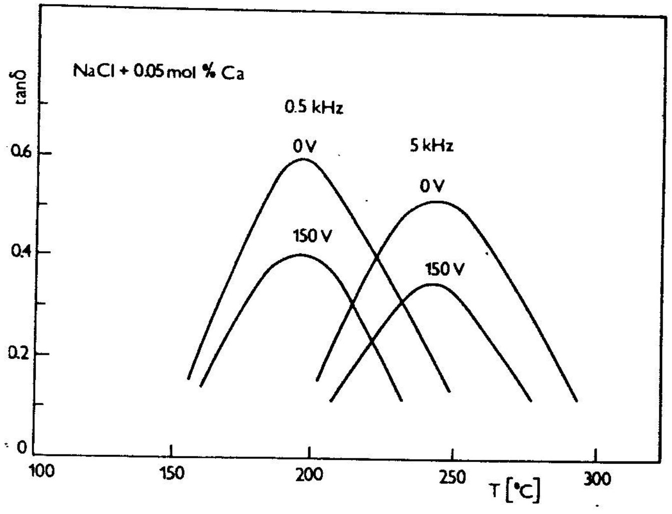

Fig. 5. Relative heights of peaks derived from graphical interpolation of conductive components of tan δ.

Figures 1—6 show the variations of tan δ, and capacitance under a.c. conditions and with the d.c. superimposed.

Figures 1—4 show that the superimposed d.c. voltage always causes a decrease in the value of the tan δ peak and an increase in the conductive component of tan δ at higher temperatures.

Figures 2 and 3 are obtained by subtracting the conductive component interpolated from the positions of the curve occurring before and after the peak from the peaked curve.

III. ANALYSIS

We assume different electric conductivities for the ionic crystal and the thin interfacial layer between the sample and the electrodes. The interfacial layer and sample conductivities increase exponentially with temperature. At lower temperatures the conductivity of the sample is smaller than that of the interfacial layer, the later does not act as a barrier to the charge carriers. With increasing temperature the total current flowing through the system is limited by the conductivity of the interfacial layer, where the increasing amount of carriers form the crystal tend to accumulate. The original 'free' carriers from the crystal in front of the interface form the interfacial polarization. Its influence on the value of tan δ is variable

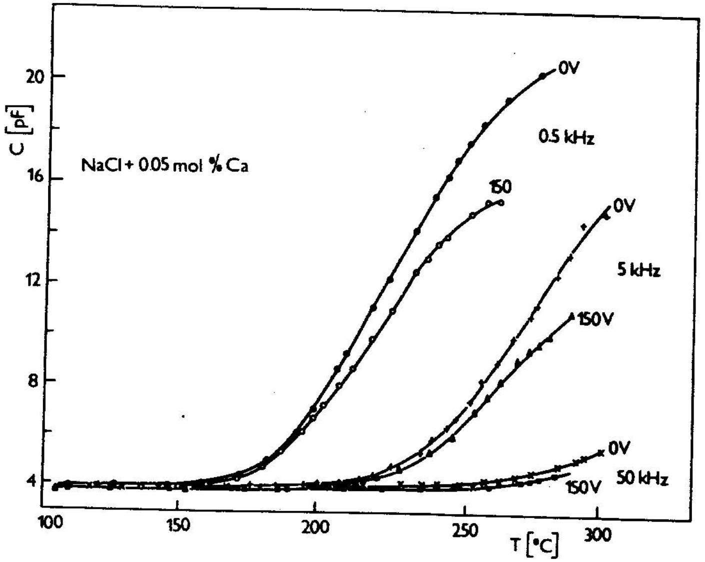

Fig. 6. Temperature dependence of capacitance at marked frequencies without and with superimpsosed d. c. voltage.

according to the mutual ratio of the components I_c, I_v, I_p and the different values of δ_p at different temperatures, as shown in figures 7 and 8.

The current I_c includes the components from the rapid polarizations which are lossless in our temperature and frequency region.

If we admit the possibility of an electron injection in the high temperature region, the increase in I_w, Fig. 7 and 8, would lead to an increase in tan δ. This possibility will be discussed in paper [15].

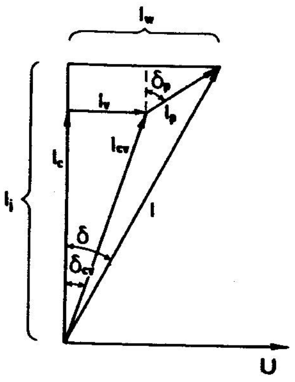

Fig. 7. Vector diagram of currents flowing across dielectric, case when I_p increases δ, $\delta_p > \delta_{cv}$.

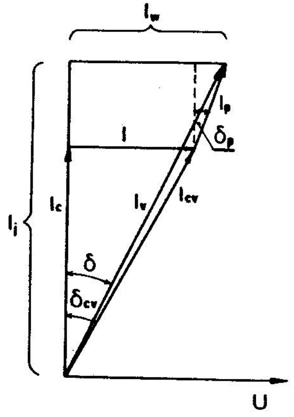

Fig. 8. Vector diagram of currents flowing across dielectric, case when I_p decreases δ, $\delta_p < \delta_{cv}$.

Part of the current, I_v, due to mobile vacancies flows across the interface and part I_p is blocked and accumulates at the interface. The zero value of I_p is blocked and accumulates at the interface. The zero value of I_p occurs slightly later than the a.c. voltage maximum, the delay being due to the inertia of the moving ions. This delay time t_p is proportional to the relaxation time of polarization, which is an exponential function of temperature:

$$\tau = \tau_0 \exp(W/kT). \tag{1}$$

W is the activation energy, T the absolute temperature.

The angle δ_p (Figs 7 and 8) depends on the delay of the polarization current I_p to the capacitive current I_c as follows

$$\frac{\delta_p}{\pi} = \frac{t_p}{T/2}, \tag{2}$$

where T is the periodic time, i.e.

$$\delta_p = \omega t_p. \tag{3}$$

The character of frequency dependencies of tan δ and C is described by equations derived from Maxwell—Wagner double-layer capacitors [16]. The real and imaginary parts of complex permittivity of dielectric with interfacial polarization are:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{4}$$

$$\varepsilon'' = \frac{\varepsilon_\infty \tau}{\omega \tau_1 \tau_2} + \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{5}$$

where $\tau_1 = R_1C_1$ and $\tau_2 = R_2C_2$.

The temperature dependence is implicitly included in the relaxation time τ, which decreases with temperature as (1), in the resistance of layers R_1 and R_2, which decrease with rising temperature, and in static permittivity ε_s, which increases with rising temperature caused by an increase of concentration of ions released from the lattice.

ε_∞ — permittivity at the frequency $\omega \to \infty$ is independent of temperature.

From equations (1, 4, 5) it can be seen that tan $\delta = \varepsilon''/\varepsilon'$ will have a peak value as the temperature increases. This may be compared with the well-known peak which occurs with the changing frequency ω. The peak in tan δ versus T was observed in previous experiments [8, 9, 11]. Our work will explain the influence of the d.c. voltage on tan δ and the capacity of the dielectric with interfacial polarization.

In the present paper we want to show how the changes of dielectric properties of the system: sample-interface-electrode caused by the superimposed d.c. voltage can be explained by assuming the decrease of I_p. The d.c. field decreases the polarization current I_p by consuming some of the carriers by the d.c. conductivity. The component I_v is limited by the low conductivity of the interfacial layer and is not influenced by the d.c. voltage.

III. THE ANALYSIS OF DEPENDENCES OF tan δ ON THE d.c. VOLTAGE

The resulting current flowing across the dielectric, I, is a vectorial sum of the currents: capacitative I_c, conductive I_v and polarization I_p in complex plane.

As rotating vectors, I_c, I_v and I_p have equal vectorial velocities, the relative positions do not change and the value of the resultant vector of their sum, which rotates with the same angular velocity, does not change.

$$I = (I_v + I_p \cos \Theta_p) + j(I_c + I_p \sin \Theta_p) \tag{6}$$

$$I = (I_v + I_p \sin \delta_p) + j(I_c + I_p \cos \delta_p) \tag{7}$$

$$\tan \delta = \frac{I_w}{I_i} = \frac{I_v + I_p \sin \delta_p}{I_c + I_p \cos \delta_p} \tag{8}$$

I_w is the total watt component of current; I_i is the total watt-less component of current; Tanδ is the dielectric loss factor. I_p is the function of temperature T and the magnitude of the d.c. voltage U, δ_p is the function of temperature described by (1 and 3). I_v and I_p are dependent on temperature as follows from the relations (10) and (11).

$$\delta = \delta_{pT_0} \exp (W/k/T) \tag{9}$$

$$I_v = I_{vT_0} \exp (-W/kT) \tag{10}$$

$$I_p = I_{pT_0} \exp (-W/kT) \tag{11}$$

I_c — the component of rapid polarizations and geometrical capacity C_0 depends on temperature only negligibly in comparison with other components of the current.

$$\tan \delta = \frac{I_{vT_0} \exp (-W/kT) + I_{pT_0} \exp (-W/kT) \sin \delta_{pT_0} \exp (-W/kT)}{I_c + I_{pT_0} \exp (-W/kT) \cos (\delta_{pT_0} \exp (-W/kT))}. \tag{12}$$

We shall investigate the dependence of tan δ upon U. In the range of low electrical fields where Ohm's law is valid it could be shown that the quantity of ions taken up by the d.c. conductivity is directly proportional to the d.c. voltage, therefore the dependence of I_p on Ushall have the general form:

$$I_{pTU} = I_{ptU=0}(1-KU), \tag{13}$$

where K is a constant at the first approximation independent from U; I_c and I_v in low electrical fields may be considered as independent of the d.c. voltage U.

By substituting the dependence of the polarization current upon the d.c. voltage (13) in (12), the form of the tanδ dependence on temperature and $U$is:

$$\tan \delta = \frac{I_{UT_0} \exp (-W/kT) + I_{pT_0U=0} \exp (-W/kT)(1-KU) \sin (\delta_{pT_0} \exp (W/kT))}{I_c + I_{pT_0U=0} \exp (-W/kT)(1-KU) \cos (\delta_{pT_0} \exp (W/kT))}. \tag{14}$$

Let us denote the components of term (14) by the following letters a_1, b_1, a_2, b_2 then

$$\tan\delta(U) = \frac{a_1U + b_1}{a_2U + b_2}. \tag{15}$$

Equation (15) is the hyperbolic function tanδ on the independent variable U [17]. Ranges of growth or decrease of the intermediate variable due to the increase of the independent variable are specified by the sign of the determinant.

$$\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} = a_1b_2 - a_2b_1. \tag{16}$$

At a low temperature where the polarization current is small and strongly lags behind the capacitive current, we have

$$\sin \delta_p > \cos \delta_p \quad \text{i.e.} \quad a_1 < a_2 \tag{17}$$

$P \to 0$ and the conductive current is small in comparison with the capacitive current

$$I_v < I_c \quad \text{i.e.} \quad b_1 < b_2 \tag{18}$$

Therefore

$$a_1b_2 < a_2b_1 \tag{19}$$

the value of the determinant is negative and therefore the function tan $\delta(U)$ is decreasing as U increases. For a positive determinant the function will increase since at a higher loss angles

$$a_1b_2 = a_2b_1. \tag{20}$$

Thus the limiting condition for the change of the characteristic dependence of tan δ_p on U is given by the equation

$$KI_p \sin \delta_p(I_c + I_p \cos \delta_p) = KI_p \cos \delta_p(I_v + I_p \sin \delta_p), \tag{21}$$

i.e.

$$\tan\delta_{p\text{crit}} = \frac{I_v + I_p \sin \delta_p}{I_c + I_p \cos \delta_p}. \tag{22}$$

The numerator of this relation is the watt component of the total current, the denominator is its watt-less component and so the limiting value for changing the sign of the determinant is the angle δ_p equal to the total loss angle δ (see relation 8). If tan $\delta_p >$ tan δ. i.e. $\delta_p > \delta$, then $a_1b_2 < a_2b_1$ and the function tan $\delta(U)$ is a decreasing function.

If tan $\delta_p <$ tan δ, i.e., $\delta_p < \delta$, then $a_1b_2 > a_2b_1$ and tan $\delta(U)$ is an increasing function.

Next let us assume the temperature to be the independent variable. The angle δ_{cv} of the components I_c and I_v increases with an increase of temperature. If δ_{cv} is equal to δ_p at the same temperature, there is a change in the quality of the effect of U on the total angle δ.

The angle δ_p is dependent on the inertia of the particles, on the temperature, but independent of U. Only the absolute value of I_p is dependent on U.

We started with the assumption that the d.c. voltage U decreases the magnitude of the polarization current and through it we elucidated with the help of the given mathematical analysis, why this monotonical influence of U on I_p causes a nonmonotonic change of tan δ. The d.c. voltage decreases tan δ if $\delta_p > \delta_{cv}$, and increases it if $\delta_p < \delta_{cv}$. The boundary of the opposite effect depends on the total ratio of the components I_c and I_v. This ratio as a consequence of the increase of I_v with temperature changes very rapidly. The temperature where the determinant of the dependence tan δ on U (relation 19) is equal to zero, i.e. $\delta_p = \delta_{cvU=0}$, is shifted by changing the frequency, which is caused by the dependence of δ_p on frequency.

In Fig. 7 there was shown a case of $\delta_p > \delta_{cv}$, in Fig. 8 $\delta_p < \delta_{cv}$. It can be seen that in the second case the addition of I_p decreases the total angle δ. Therefore the decreasing of the absolute value of I_p by U changes the total angle δ in two ways. In the low temperature region, where $\delta_p > \delta_{cv}$, the component I_p increases the total angle δ and therefore the decrease of I_p by U decreases the total $\tan\delta$. In the higher temperature region, when $\delta_p < \delta_{cv}$, the component I_p decreases the total angle δ. Therefore there the decrease of I_p by U increases the total angle δ.

The influence of the d.c. voltage on the variation of capacitance with temperature is shown in Figs. 3 and 6.

The capacitance of the dielectric system is proportional to the capacitive (watt-less) components of the currents I_c and I_p, i.e. $I_c + I_p \cos\delta_p$. The I_p increases with temperature because a large number of ions is freed from the lattice and becomes available for conductivity and polarization. Also the mobility of ions rises and therefore δ_p decreases and $\cos\delta_p$ increases. The capacitive component of the current and therefore also the capacity increase with temperature. By increasing U the total capacitance decreases as a consequence of decreasing I_p since the other components remain unchanged.

IV. CONCLUSIONS

The aim of this work was to ascertain and explain the change of values of the capacitance and the loss factor influenced by superimposition of d.c. and a.c. voltages on the dielectric system: electrode-interface of imperfect contact-sample of a single crystal of NaCl.

We applied the mechanism of interfacial polarization and the influence of d.c. voltage on the polarization current I_p. The changes of the absolute value and the phase shift of I_p on the values of C and $\tan\delta$ of the dielectric system were studied.

This system was investigated as a model for layered dielectric structures applied in industry, which show changes of dielectric properties after superimposition of a d.c. to a a.c. voltage. The qualitative and quantitative analyses explain why the d.c. voltage decreases the capacity of the system and why $\tan\delta$ increases or decreases according to certain conditions determined by the relation between the phase angle of the current from the single interfacial polarization and the phase angle from the conductive and capacitive current.

We suppose that the analysis of the problem and the conclusions of this work could help to explain the behaviour of combined dielectrics (consciously planned or unconsciously of several layers) when the simultaneous action of a.c. and d.c. voltages is present.

Finally it can be commented that the analysis manifests one advantage of multilayer structures. The polarization current at higher temperatures, when its delay is shorter, decreases the total angle δ in comparison with conditions when the watt current flowing accross the dielectricum was only conductive.

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