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ACCURATE DETERMINATION OF DIELECTRIC PROPERTIES

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Accurate Determination of Dielectric Properties

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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ACCURATE DETERMINATION OF DIELECTRIC PROPERTIES

Abstract

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CARL GUSTAV ANDEEN

A systematic effort has been made to obtain accurate values for several dielectric properties of insulating crystals. The dielectric properties of interest are the static dielectric constant (the SDC), the pressure dependence of the SDC, the temperature dependence of the SDC, and the frequency dependence of the SDC.

This work has resulted in a technique, the method of substitution, which obsoletes all previous methods for determining the SDC. The pressure dependence of the SDC has been used as the basis of a highly accurate pressure gauge. Preliminary results for the temperature dependence of the SDC have led to an extension of this work into the investigation of impurity effects on dielectric properties.

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I. Introduction

A few years ago the pressure derivatives of the elastic constants of CaF_2 and BaF_2 were measured by C. Wong¹ at this laboratory. The present work was started as an attempt to complement his results with accurate values for the pressure derivatives of the static dielectric constant (SDC) for the same materials.

Since previous investigations^{2,3,4,5,6} of dielectric properties had shown a disturbing amount of scatter and lack of agreement, a considerable effort was made to remove every possible source of random and systematic errors. Initially this involved the refinement of conventional measuring apparatus and techniques, but has evolved into a comprehensive program allowing the accurate determination of several dielectric properties.

A new technique, the method of substitution,⁷ has been developed and used to obtain results for the SDC of several ionic crystals with an accuracy of 0.01%, fifty times better than the previous limit of 0.5% using geometrical methods.⁸

The measurement of the pressure dependence of the SDC has been improved to the level where eight crystals of CaF_2 , obtained from the Harshaw Chemical Company, have been taken to the National Bureau of Standards and calibrated as secondary pressure standards. The spread in the pressure coefficients of capacitance for the eight crystals was actually less than the stated inaccuracy of the dead weight gauge against which they were calibrated.

Absolute measurements for the temperature dependence of the SDC have been limited by uncertainties in the reference thermometer.

However, the simultaneous observation of the capacitance of several samples during a temperature run indicates a high degree of reproducibility in the capacitance and also allows the observation of low-level impurity effects on the SDC. These impurity effects, which are characterized by an activation energy and a unique relation between dielectric loss, frequency and temperature, should be a powerful tool for studying the dielectric properties of crystals, and may also be useful for analysis of impurities in insulating crystals. To exploit this possibility a capacitance bridge has been designed that will allow accurate measurements of dielectric properties over the entire frequency range from 33.33 Hz to 100 kHz.

This capacitance bridge, which is nearing completion, together with a new NBS-certifiable platinum resistance thermometer should allow the measurement of the temperature dependence and frequency dependence of the SDC at the same high level of accuracy as that obtained for the pressure derivatives of the SDC and for the SDC itself.

II. Accurate Determination of the SDC

The method of substitution has been developed to obtain accurate values for the SDC of insulating crystals. This method, along with associated refinements in the experimental apparatus, is discussed in Reference 7. The important features of this method are that it requires no geometrical measurements, there are no electrodes applied to the sample, and the samples come in contact only with relatively inert liquids or air. It should also be noted from the initial results of the method that there is no significant effect due to sample thickness, choice of immersion liquids, or substitution cell material.

Results of a rather extensive investigation into the SDC of several alkali halide crystals are included in Reference 13. The excellent agreement in most cases between crystals of the same material obtained from different manufacturers should be stressed, as well as the lack of orientation dependence and the inherent uniformity in the results for the SDC of Harshaw lab-pack NaCl crystals.

In Reference 14 are included the preliminary results for the SDC of the cubic alkaline earth fluorides. Of major interest here is the large variation in the SDC and a corresponding variation in the dielectric loss of Optovac CaF_2 crystals. This variation, together with the spread in the results for the SDC of SrF_2 obtained from Harshaw and Optovac, forms the basis for an extension of this work into the effects of impurities on the SDC. This will be considered in more detail in a later section dealing with the temperature dependence of the SDC.

III. The Pressure Dependence of the SDC

By using the method of substitution it is now possible to obtain an accurate result for the SDC of most insulating crystals. However, the real value of obtaining this accurate result for the SDC is in its use as the starting point in mapping the SDC surface as a function of pressure and temperature, and for determining the perturbations of this surface with frequency and impurity content. Since all of the values for the SDC which are reported in References 7, 13, and 14 were obtained at 300°K, 1 bar, and 1 kHz these conditions are taken as the reference point. Once the SDC is determined at this reference point it is possible to map the remainder of the SDC (P,T,f) surfaces by a more conventional approach involving the application of electrodes directly onto the sample.

These electrodes must be applied to the sample in such a manner that they form a three-terminal capacitor with the sample as the dielectric. In previous work^{2,3,4,5,6,8} the electrodes have been painted on with conductive paint, deposited from thermally decomposing organic paints such as organic silver and organic platinum, or vacuum-evaporated to form a thin film of aluminum, gold, or other non-reactive metal. The necessary gap between the guard electrode and the center electrode has been obtained either by scribing the surface or, in the case of the evaporated films, by using a suitable "shadow ring" to produce a narrow annular gap in the conductive film. Neither of these methods has been very successful in the past and therefore they were not used in the present work.

A different technique for depositing these electrodes has been developed which involves three separate evaporations to form the three required electrodes. The guard electrode is evaporated first, resulting in a fairly wide annular ring. The center electrode is then evaporated after carefully positioning the sample under a suitable mask, the inside diameter of this mask determining the resultant gap width between the center electrode and the guard electrode. The opposite face of the sample is then evaporated as the final step. With this technique it is possible to achieve a well-defined guard gap as narrow as 0.0005" in width.

Results for the pressure derivatives of the SDC for several alkali halide crystals with electrodes deposited in this manner are reported in Reference 9. Of particular interest is the fact that with this technique it is now possible to obtain values for the third derivative in the pressure dependence of the SDC.

Initial measurements of the pressure dependence of the SDC obtained for Harshaw CaF_2 crystals were so reproducible that this material was subsequently developed into a highly accurate pressure gauge sensor. Background information specifically applicable to the use of CaF_2 as a pressure gauge sensor, together with further details of the evaporation technique, is contained in Appendix I.

Results of a pressure calibration performed at the National Bureau of Standards on eight crystals of CaF_2 , which were prepared using these techniques, are reported in Reference 15. From the result that the gauge constants for the various CaF_2 crystals agreed within one part in 20,000 it becomes quite clear that CaF_2 does indeed make

a good pressure gauge sensor. It is also obvious that the problems associated with previous investigations into the pressure dependence of the SDC have been solved to a remarkable degree.

IV. The Temperature Dependence of the SDC

Preliminary results for the temperature dependence of the SDC of several alkali halides have been obtained and are reported in Reference 9. However, the accuracy of these results is limited to approximately 0.1 C° by hysteresis in the platinum resistance reference thermometer (PRT). The present PRT, which has a 0°C resistance of 1000 ohms, is being replaced with a larger PRT having a 0°C resistance of 25 ohms. This 25 ohm PRT is made to conform with NBS specifications, and should appreciably improve the temperature accuracy in the measurements of the SDC. The modifications in the instrumentation which will be required because of this new thermometer are sufficiently extensive that the existing temperature control system will not be discussed in detail, as had been promised in Reference 9.

In spite of the observed hysteresis in the PRT, it has been possible to extract very good data for the effect of impurity contributions to the SDC. This was done by monitoring the ratio between the capacitances of two samples of the same material, one containing an impurity and one nominally pure.

Figure 1 shows the results of one such run obtained by using a crystal of Harshaw SrF_2 as the "pure" crystal, and a crystal of Optovac SrF_2 as the impure crystal. The observed change in the ratio of the capacitances is plotted as a function of temperature over the range from 80°K to 320°K, together with the corresponding difference between the observed dielectric losses for the two samples. Also contained in Figure 1 are calculated curves which were obtained

by best-fitting to a simple schematic model which is given in Figure 2. This model explains both the observed shape of the loss peak and the decrease in the capacitance enhancement as the temperature is increased beyond the critical region.

An interesting observation can be made from the above results. Although the maximum capacitance enhancement amounts to only 600 ppm (0.06%) and at room temperature is only 0.05%, in the vicinity of the loss peak there is actually an increase of 13% in the temperature derivative of the SDC for the impure sample relative to that of the pure sample.

By repeating these measurements at several different frequencies it is possible to shift the temperature at which the loss peak occurs and thereby obtain meaningful data for the temperature dependence of the SDC, even in the presence of a large ionic conductivity which would obscure the loss peak. For this reason the measurements of dielectric properties have been extended to include the frequency dependence of the SDC, and a capacitance bridge has been designed specifically for the purpose of obtaining accurate results for dielectric properties over as wide a frequency range as possible.

Figure 1.

Observed loss peak in impure SrF_2 (Optovac) and resultant capacitance enhancement. (Measured relative to Harshaw SrF_2 with $f = 1$ kHz). Dashed curves - Loss peak and capacitance enhancement calculated from schematic model. (Calculated curves are displaced upward for clarity).

IMPURE CRYSTAL

PURE CRYSTAL

Figure 2. Schematic Model for Impurity Contribution to the SDC.

V. The Frequency Dependence of the SDC

A close examination of the schematic model given in Figure 2 reveals that the total effect of any one impurity on the SDC can be characterized by three fitting parameters. At some reference frequency there is a maximum value for the dielectric loss versus temperature. This loss maximum occurs at some well-defined temperature, and the width of this loss peak is uniquely determined by the activation energy associated with the loss mechanism. By using these fitting parameters it is possible to predict curves for the SDC versus temperature and dielectric loss versus temperature over a wide range of frequencies. Comparison of these curves with observed data is useful both as a test of the schematic model and as a means of separating the contributions from several different impurities.

Figures 3 and 4 were obtained by fitting the observed parameters for the impure Optovac SrF_2 at each of the eight discrete frequencies to be covered by the newly designed capacitance bridge. The shift in the temperature at which the maximum loss occurs depends on the activation energy of the loss mechanism. If there are two or more impurity contributions with different activation energies they should be separable by observing the dielectric loss versus temperature at several different frequencies. By repeating these measurements on grossly impure samples, whose impurities can be determined analytically, it should be possible to relate the observed low level impurity contributions to actual impurities or defects, thereby allowing the identification of impurities in supposedly "pure" crystals.

Figure 3.

Dielectric loss versus temperature calculated from schematic model using same fitting parameters as Figure 1. The frequencies are those of the capacitance bridge which is under construction, 10^n Hz and $(10^n)/3$ Hz from 33.33 Hz to 100 kHz.

Figure 4.

Impurity capacitance enhancement versus temperature calculated from schematic model using same fitting parameters as Figure 1. The frequencies are the same as in Figure 3.

VI. A Capacitance Bridge for the Accurate Determination of Dielectric Properties

The results for the SDC which are reported in References 7, 9, 13, and 14, were all obtained using a modified General Radio 1620-A Capacitance Measuring Assembly which was operated at 1 kHz. At this frequency the setup is capable of obtaining meaningful results at the one ppm level, but as the frequency is changed more than a factor of three above or below 1 kHz the performance deteriorates rapidly. At low frequencies the bridge voltage is limited by saturation of the transformer core, and consequently the sensitivity is reduced. At high frequencies the combined effects of leakage reactance and capacitive loading effects in the transformer winding, together with capacitive loading due to the necessary cables and auxiliary apparatus limit the usefulness of the setup to the frequency range from 300 Hz to 3 kHz, a factor of only ten. Since the separation of impurity effects and testing of the schematic model require as wide a frequency range as possible, it was considered worthwhile to design a capacitance bridge specifically for the accurate measurement of dielectric properties.

This has been attempted only because a similar bridge, operating at 2005 Hz, had previously been designed and constructed at this laboratory. This capacitance bridge was used for all of the measurements on the CaF_2 pressure gauge sensors and was capable of obtaining meaningful results at the 1/10 ppm level.

Virtually all audio frequency capacitance measurements which claim any accuracy are done using three-terminal capacitance

techniques together with a ratio transformer in some type of bridge circuit. A simplified bridge circuit is shown in Figure 5a. It should be obvious that bridge balance occurs when $I_1 = I_2$ so that $I_3 = 0$, and for this example bridge balance requires $V_1/Z_x = V_2/Z_s$ (where Z_x and Z_s are the complex impedances of the unknown and standard, respectively). The various bridges and ratio transformers differ mainly as to how V_1/V_2 is obtained and what type of standard (Z_s) is employed.

In Figure 5b is a basic diagram for the General Radio 1620-A Capacitance Measuring Assembly. For this configuration the voltage across the unknown is fixed and various 10 pf, 1 pf, 0.1 pf, etc. standards are connected to suitable taps on the reference side of the transformer. Since for a lossless capacitor $Z = -jX_c = -j/\omega C$ the bridge balance equation can be written as

$$V_1 j\omega C_x = V_2 j\omega C_s$$

or

$$V_1 C_x = V_2 C_s$$

which involves capacitance directly.

Assuming an unknown capacitance of 7.3000 pf, bridge balance would occur with the 10 pf standard connected to the 0.7 tap, the 1 pf standard connected to the 0.3 tap, and all other internal standards connected to the 0.0 tap.

$$\text{Thus } VC_x = 0.7V \times (10.0000) + 0.3V \times (1.0000) + 0 \times (0.1....)$$

$$\text{and } C_x = 7.300...pf$$

Figure 5.

- (a) Simplified bridge circuit.
- (b) Basic diagram for the General Radio 1620-A Capacitance Measuring Assembly.
- (c) Basic diagram for a capacitance bridge using a commercial ratio transformer.

SIMPLIFIED BRIDGE CIRCUIT

BASIC DIAGRAM OF GR 1620-A BRIDGE

RATIO TRANSFORMER BRIDGE

This configuration is convenient because of its simplicity. Only one transformer, tapped at intervals of $0.1V_{\max}$ is required. However, this method requires multiple internal capacitance standards and has several drawbacks when wide frequency operation is desired. Even though adjacent decades of the internal standard capacitors can be calibrated rather easily after an initial check against a reference capacitor, the loss of these internal standards is in general not uniform, and neither the loss nor the capacitance of these internal standards is constant with frequency. Thus, if accurate measurements are required over a wide frequency range, this arrangement leaves much to be desired.

A circuit using one of the many commercial ratio transformers^{10,11} is shown in Figure 5c. A rather serious disadvantage of this method is the indirect relation between unknown capacitance and indicated ratio. Since the total voltage across the transformer is constant the ratio between the two arms of the bridge is actually $x/(1-x)$, where x is the indicated ratio. Also, most commercially available ratio transformers are optimized at a frequency of 1 kHz and consequently have rather large winding resistance and leakage reactance which limit their use above 3 kHz. This effective output impedance also varies with the setting of the ratio controls, thereby causing some rather insidious errors in the observed ratio.

The ratio transformer used in the 2005 Hz bridge developed for the pressure gauge measurements was actually a modification of the commercial ratio transformers. Since all of the pressure gauge sensors and the temperature-controlled reference capacitors have

approximately the same capacitance it was possible to make a limited-range ratio transformer. The main winding was divided into nine equal divisions instead of the usual ten. The second decade was permanently connected across the fifth division as shown in Figure 6. This connection only allows the measurement of ratios between $4/5$ and $5/4$, which was sufficient for the pressure gauge work, but unity ratio conveniently occurs at the middle of this range. If ten divisions had been chosen for the first winding, unity ratio would have occurred right at the fifth step and small deviations on either side of unity would have required moving the second transformer to a different division of the main winding.

The effective impedance of the fifth division of the main winding was lowered significantly by connecting four equivalent sections in parallel, thereby allowing a lower impedance for the second transformer without seriously loading the main transformer. This redundancy, together with the permanent connection of the second transformer across the fifth division, drastically reduced any tendency for the output impedance to change with dial setting, thus effectively eliminating the "insidious" errors mentioned previously.

A further improvement in the operation of this 2005 Hz capacitance bridge was made possible by virtue of its single frequency operation. The discrepancy between the measured ratio and the actual ratio can be determined by means of a "bootstrap" technique,¹² and it is possible to "trim" the various tenths and hundredths divisions with suitable resistors and capacitors to reduce this discrepancy. With a repeated application of this rather tedious

2005 HZ LIMITED - RANGE BRIDGE

Figure 6. Limited-range 2005 Hz capacitance bridge used as a pressure gauge in conjunction with CaF_2 pressure sensors.

technique the errors can be made as small as desired. The 2005 Hz bridge ratio transformer was trimmed using this method until the discrepancy was reduced to less than 1 part in 90,000,000 of the total voltage across the transformer. Obviously this trimming is correct only at a single frequency and is impractical to apply to a ratio transformer which will be used over a range of frequencies.

The ratio transformer configurations shown in Figures 5 and 6 have been considered in some detail because they lead in a logical way to an improved design which offers the best features of each type.

The setup shown in Figure 5b uses a simple transformer but requires multiple capacitance standards, a disadvantage in the present work. It does, however, have the advantages that it is direct reading and that the voltage across the unknown is independent of dial setting. The ratio transformer shown in Figure 5c is awkward to use since the unknown capacitance must be obtained from the indirect relation $C_x = C_s x/(1-x)$. Also, the voltage across the unknown varies with the ratio setting. However, by limiting the range of the ratio transformer as is done in Figure 6, this voltage effect can be made relatively unimportant. Finally, by suitable winding redundancy it is possible to minimize output impedance variations by a significant factor. This also was done in Figure 6.

A design for a ratio transformer which combines most of the desirable features of the previous types is shown in Figure 7. By splitting the winding as shown it is possible to apply redundancy

1 KHZ - 3 KHZ RATIO TRANSFORMER BRIDGE

Figure 7. Modified design for a ratio transformer to be used in a newly designed high accuracy capacitance bridge.

to the secondary winding while at the same time preserving direct readout of capacitance and maintaining constant voltage across the unknown capacitor. Also, only one capacitance standard is required.

A further improvement over commercial ratio transformers can be achieved by lowering the ratio transformer design voltage to the point where random errors due to electronic noise fluctuations are roughly equal to systematic errors in other parts of the overall system. By lowering the transformer design voltage it is possible to obtain a large reduction in the effective output impedance of the ratio transformer, thereby reducing associated systematic errors which in practice are far more significant than the readout limitation due to random noise in the electronic detector.

As an example, most commercial ratio transformers are limited by saturation of their core to operating voltages below 0.35 f(Hz) volts, which allows a maximum voltage of 350 volts at 1 kHz. To achieve this large voltage capability requires that the core be wound with many turns of rather fine wire, consequently the resistance and leakage reactance of these commercial ratio transformers are both quite large.

If the design voltage were decreased by a factor of ten, then only one-tenth as many turns would be required and each of these turns could have ten times the cross sectional area of the original turns. The effective resistance of this winding would then be lower by a factor of 100 relative to the original, and by proper winding the reactance would be comparably improved. Thus by reducing the transformer design voltage the systematic errors due to bridge

loading, variations in this load, or due to changes in the ratio transformer dial setting can be reduced to almost any desired level, but at the same time care must be taken so that random errors don't cancel this improvement.

From observations made on both the 1620-A setup and the 2005 Hz bridge a design voltage of 8 volts at 1 kHz was determined as being optimum for the present capacitance bridge. At this voltage the uncertainty due to thermal agitation noise in the input circuit sets a lower limit of $\approx 10^{-6}$ pf in the capacitance resolution obtainable in reasonable observation times (a few seconds).

A ratio transformer with 8 volts across each half of the secondary winding was wound as shown in Figure 7. The resistance, reactance, and interwinding capacitances were sufficiently low that this same transformer was also acceptable at 3.333 kHz, (this odd frequency $(10^n)/3$, rather than 3×10^n , being chosen to avoid interference from 60 Hz power circuits which would occur at 30 Hz and 300 Hz). However, this 1 kHz transformer was not acceptable for use at 10 kHz, and consequently another transformer was wound for the frequency range of 10 kHz and above. The most important requirement for this 10 kHz transformer is a low value for the interwinding capacitances, since the effect of the distributed capacitance in each winding can be largely corrected for by suitable trimming. The resulting transformer should allow measurements to 1 part in 3×10^6 at 10 kHz, 1 part in 1×10^6 at 33.33 kHz and 1 part in 2×10^5 at 100 kHz.

The 1 kHz transformer is obviously unsuitable for lower frequencies because of core saturation. A third ratio transformer was therefore wound for 33.33 Hz, 100 Hz and 333.3 Hz. This transformer was wound on the core from a Powerstat autotransformer. This core has a large cross sectional area and a high value for its maximum flux density, both of these factors reducing the number of turns required to achieve a reasonable voltage at 33.33 Hz. Also, by minimizing the number of turns the performance at 333.3 Hz is improved. The final low frequency transformer has 100 turns in each half of the secondary winding, and therefore it is possible to use one transformer for two sections of the decade divider.

Each of these ratio transformers forms the front end of a six decade transformer divider. Because this front end is the most critical part of the divider it has been necessary to use three different ratio transformers to cover the required frequency range. Fortunately, the accuracy of the voltage division in the remaining decades is less demanding and it is possible to use one five decade divider to complete the middle and high frequency ranges, and one four decade divider can be used to complete the low frequency range. The desired voltage division accuracy can be achieved by trimming the individual steps of the first few decades as was done for the 2005 Hz ratio transformer. However, there is no easy way to achieve a low output impedance, especially at high frequencies.

The final design for the five decade divider involved fifteen separate toroidal divider transformers in three parallel arrays of five dividers each. Each of the fifteen transformers has at least

sixty separate windings to allow adequate distribution of the windings around the core in order to obtain a sufficiently low value for the leakage reactance of each transformer. As an example, the last decade required only one turn per step to obtain acceptable voltage division, a total of ten turns. The final transformer design for this decade used eighty separate windings of one turn each, arranged so that each step of the decade was actually eight separate windings, uniformly spaced around the toroid and connected in parallel. In this way the resistance and leakage reactance of each transformer were reduced as much as was reasonable. By connecting three of these transformers in parallel, as was done in the final array, the resistance of this last decade was reduced to less than 0.002 ohms and the inductance to less than 0.02 microhenry, for any position of the associated selector switch. This corresponds to a maximum effective output impedance, for the last decade, of $(0.002 + 0.012j)$ ohms at 100 kHz and only 0.002 ohms at 1 kHz.

The remaining decades of the five decade divider were treated similarly, so that regardless of the positions of the selector switches the output impedance of this divider never varies by more than 0.02 ohms in resistance or 0.15 microhenry in inductance. With this divider connected to the 10 kHz ratio transformer the resulting six decade divider has an output impedance which is never higher than 0.05 ohms and 0.20 microhenry. This corresponds to $(0.05 + 0.012j)$ ohms at 10 kHz, $(0.05 + 0.04j)$ ohms at 33.33 kHz, and $(0.05 + 0.12j)$ ohms maximum at 100 kHz. Assuming a capacitive load of 100 pf, which would have an impedance of $-16,000j$ ohms at 100 kHz,

there would be an error at this frequency of less than 1 part in 10^5 due to the voltage drop in the output impedance. At 33.33 kHz the capacitive loading would be only one-third as large and the inductive reactance would be decreased by a factor of three with a resulting improvement in the error to approximately 1 part in 10^6 .

An important consideration should be stressed here. Since most of the measurements for the pressure and temperature dependence of the SDC involve relatively small changes in the SDC, in general only the last several decades are changed during a run. These last decades can be made to have a very small impedance variation, with the result that their effect on the observed error will be very small. This allows an incremental precision and accuracy, especially for small changes, which are several times better than the overall accuracy, and in practice this effect is quite significant. To fully utilize this incremental precision, each six decade divider has been designed to allow trimming to an accuracy of one-tenth of a step in the last decade over its entire frequency range. This should allow measurements with a precision of one part in several million.

These six decade dividers, which form the ratio transformer divider section of the capacitance bridge are obviously capable of excellent performance over quite a wide range of frequencies. However, the resulting capacitance measurements will be no better than the limitations due to the reference capacitor. A General Radio 1404-C 10 pf Reference Standard Capacitor has been chosen for this reference capacitor. This capacitor has a dielectric of dry N_2 gas, and should therefore have very little variation in its capacitance

over the desired frequency range. Since the reference capacitor is 10 pf the capacitance bridge will have an optimum range of 0-10 pf, which is ideal for the SDC measurements, and the loading effect on the ratio transformer will be very small compared with the loading from a 100 pf reference capacitor. The reference capacitor will be removed from its mounting plate to reduce its already low inductance and will be placed in a thermostatically-controlled oven. This oven will be controlled to 0.01°C and will be located in close proximity to the ratio transformer dividers to minimize lead inductance. Any residual dissipation factor and frequency dependence in this reference standard capacitor will be common to all measurements taken with the capacitance bridge and should show up as a consistent perturbation in the results.

VII. A Low Frequency Capacitance Bridge

The bridge which has been described was designed to allow accurate measurements of capacitance over as wide a frequency range as possible. At the high frequency end of this range (100 kHz) the inductance and capacitance associated with connecting cables and feedthroughs into a pressure vessel or leads into a controlled-temperature cryostat are absolute limiting factors which rule out any extension of this range to higher frequencies. The substitution cell presently in use for the measurement of the SDC is limited by its design to a frequency range of 3 kHz or lower, with optimum results at 1 kHz or less. At the low frequency end of the range the voltage capability of the ratio transformer is limited by core saturation, and at the same time the absolute sensitivity of the detector is reduced by its input circuitry. In this bridge, which covers the frequency range from 33.33 Hz to 100 kHz, the detector input is tuned with a high Q inductor to reduce the loading effects of cable and circuit capacitances. At very low frequencies it is impossible to obtain a sufficiently high inductance to be optimum for this purpose. For example, at 33 Hz it would be desirable to use an inductance of 20,000 henries to resonate with the circuit capacitance of ≈ 700 pf. Unfortunately, a coil having this much inductance would also have a large distributed capacitance and because of the low frequency would also have a low Q. The net result is that the effective impedance at a detector with a tuned input is difficult to increase beyond 10 megohms at 33 Hz or lower. At

resonance this is a resistive impedance and consequently represents a noise source equivalent to ≈ 10 megohms. The combined effects of the transformer and detector limit the low frequency operation to 33.33 Hz, and at this frequency the sensitivity is marginally acceptable when accurate measurements are desired.

To extend the frequency range to much lower frequencies another capacitance bridge has been designed specifically for the frequency range from 1 Hz to 100 Hz. This capacitance bridge differs from the 33.33 Hz to 100 kHz bridge in that it uses an untuned FET input which is bootstrapped in a simple way to achieve an input impedance of as much as 10,000 megohms. This allows adequate detector sensitivity at frequencies as low as 1 Hz. A large Powerstat autotransformer core, wound with 2000 turns of wire to supply the voltage across the unknown capacitance, has been used for the ratio transformer. With this ratio transformer it is possible to maintain a voltage of 30 volts across the unknown down to a frequency of 3.33 Hz, and only dropping to 20 volts at 1 Hz. A basic diagram of the ratio transformer used in this low frequency capacitance bridge is shown in Figure 8, and in Figure 9 is a schematic for the high impedance pre-amplifier used in the detector.

Figure 8. Basic diagram for a low frequency capacitance bridge covering the frequency range from 1-100 Hz.

HIGH INPUT IMPEDANCE PREAMPLIFIER (FET SOURCE FOLLOWER)

Figure 9. High impedance preamplifier to be used in the detector of a low frequency capacitance bridge covering the frequency range from 1-100 Hz.

CONCLUSIONS

The work described herein forms a solid foundation for an investigation into the dielectric properties of ionic crystals. For the first time it is possible to directly relate impurities and defects with their resultant effects on the static dielectric constant. A systematic study of the SDC of nominally pure single crystals, including the variation of the SDC with pressure, temperature, and frequency should allow the separation of impurity effects from the intrinsic dielectric properties of the pure material.

A CaF_2 pressure gauge developed in the course of this work shows promise as a highly accurate and reproducible gauge for use at high pressures, but equally as important the results from this gauge are an indication of the extremely well-defined nature of dielectric properties of single crystals.

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APPENDIX I. PREPARATION OF CAPACITIVE PRESSURE SENSORS

Introduction

In a calibration performed at the National Bureau of Standards in July, 1970 eight single crystal CaF_2 samples, each with evaporated metal film electrodes forming a three-terminal capacitor, were calibrated over the pressure range from 0-35,000 psi.

A relation was found between the three-terminal capacitance at high pressure and that at zero pressure which had the empirical form:

$$C/C_0 = 1 - 2.6063 \times 10^{-7} P/(\text{psi}) + 1.302 \times 10^{-13} P^2/(\text{psi})^2$$

where P is the pressure in psi.

The major result and an indication of the inherent capabilities of the capacitive pressure sensor was that every data point from each of the eight samples agreed within 2 psi of this empirical equation over the entire pressure range 0-35,000 psi. This corresponds to a reproducibility between samples of $\pm 0.005\%$ of full scale.

The prototype apparatus which was used for this calibration consisted of the following:

1. the CaF_2 capacitive sensors,
2. a capacitance bridge and reference capacitor capable of accurately measuring very small capacitance changes,
3. a temperature-controlled pressure vessel which was specially designed for accurate measurement and control of the sensors contained within it.

A CaF_2 Capacitive Pressure Sensor

If one considers the simple formula for the capacitance of a parallel plate capacitor $C = \epsilon A/d$ (where ϵ is the dielectric constant, A is the area of the capacitor, and d is its thickness) it is obvious that to accurately define the capacitance it is necessary to accurately define ϵ , A , and d . Fortunately we are mainly concerned here with percentage changes in capacitance due to an applied pressure and it is easier to work with a simplified expression.

Since an isotropic crystal maintains its shape under hydrostatic pressure one can consider the (A/d) part of the above equation as being equivalent to $(\text{area}/\text{thickness}) = (\text{length}^2/\text{length}) = \text{length}$, so that $C = \epsilon l$ (for an isotropic crystal) and percentage changes in C due to an applied pressure or temperature change depend only on the resulting percentage changes in ϵ (the dielectric constant of the crystal), and in l (a linear dimension of the crystal), both of which are intrinsic properties of the crystal.

For the crystal which we are most concerned with (CaF_2), ϵ decreases by 4.0 parts per million per bar (1 atmosphere) and l decreases by 0.4 parts per million per bar resulting in a decrease in C of 4.4 parts per million per bar. However, ϵ and l are also quite sensitive to temperature, ϵ increasing by 240 and l by 20 parts per million per degree Celsius, which increases C by 260 parts per million per degree. From this we can see that for CaF_2 , each degree of temperature is equivalent to -60 bars (≈ 1000 psi). This necessitates somewhat elaborate temperature control.

The capacitance samples used in the prototype gauge have an effective diameter of 0.563" and a thickness of 0.062" which result in a capacitance of ≈ 6 pf. From the above considerations on the dependence of ϵ and l on P and T it is apparent that for CaF_2 a 0.01% change in P at 40,000 psi results in a change in C of ≈ 1 ppm, and consequently it is necessary to measure a capacitance of 6 pf (a rather small capacitance) with a stability and incremental precision (not accuracy) of better than 1 ppm. Since the capacitance changes will have to be measured to the part per million level it is necessary to be quite rigorous in defining the appropriate boundary conditions.

The previously mentioned equation $C = \epsilon A/d$ really represents an idealized case, a section cut out of an infinite parallel plate capacitor with no fringing field or other aberrations. As in many cases similar to this where boundary conditions are important a guard electrode can be utilized, which in this case results in a three-terminal capacitor.

In Figure 1 it is obvious that the guard electrode shields the direct capacitance between the high and low electrodes from the effects of the fringing field. If the guard electrode is chosen properly the resulting high-low capacitor simulates a section cut out of an infinite parallel plate capacitor and $C = \epsilon A/d$ applies. It can be shown mathematically that if the guard electrode width is at least three times the thickness of the sample then the effect of the fringing field is unimportant at the desired 1 ppm level. The only other aberration which is significant is the effect of the quite

Figure 1. Three-terminal capacitor.

necessary gap between the guard electrode and the low electrode. This gap allows the direct high-low capacitance to "see" the pressure fluid and therefore must be made as small as possible. In the prototype sensors this gap was less than one thousandth of an inch in width.

Boundary conditions alone rule out any shape other than a flat circular disk, but the actual dimensions of the sensor are not critical. Since much of the work in our laboratory involves pressures of less than 40,000 psi it was possible to design pressure vessels with a rather large bore (1.220"). This allows the use of samples which are relatively large and easy to work with, and therefore we have standardized on 1" diameter samples, which have the added advantage of being a standard easily available size. The thickness is a compromise between required capacitance sensitivity in the bridge and fragility of the sample. The prototype sensors have a thickness of 0.062" and with this thickness the resulting samples are sufficiently durable that no sample has ever been broken during a pressure run.

The actual dimensions of the prototype sensors are 1" O.D., 0.062" thick, with a 0.563" diameter guard gap (which results in a favorable guard ring width to sample thickness ratio of 3.5). As mentioned before these dimensions result in a three-terminal direct capacitance of ≈ 6 pf (for CaF_2). If a larger capacitance were desired the sensors could be made thinner (and thus more fragile), e.g. with a diameter of 1" and a thickness of 0.031" the guard ring width could be as small as 0.093" resulting in a 0.814" diameter

guard gap and a capacitance of over 20 pf, but the sensors would probably be too fragile to use. More likely one would wish to minimize the diameter of the sensor to allow use at higher pressures. A 0.500" diameter, 0.031" thick sensor with a guard gap diameter of 0.281" is a reasonable starting point, but the sensor would have a capacitance of only 3 pf and would be quite difficult to work with because of its small size.

It should be obvious that the sensitivity in terms of parts per million per bar is independent of the thickness or diameter of the sample (this follows from the discussion on $C = \epsilon l$).

For a sensor with the dimensions of the prototype one ppm in capacitance corresponds to a change in sample thickness of 0.06 millionths of an inch or equivalently to a change in guard gap diameter of 0.3 millionths of an inch. It is therefore absolutely essential that the electrodes forming the three-terminal capacitor make intimate contact with the surface of the crystal and that the edges of the electrodes be as sharply defined as possible. The only method which has proven successful for the deposition of these electrodes involves a three step vacuum evaporation of an aluminum film onto an optically polished sample of CaF_2 , with the sample being maintained at 150°C during the evaporations.

The CaF_2 samples were obtained from the Harshaw Chemical Co. in the form of 1" O.D. single crystal disks approximately 0.1" thick. These disks were first hand-lapped down to 0.080" thick in a steel lapping tool using Carborundum "Fastcut" paper, then they were lapped and polished in groups of five on a specially made planetary lapping

machine having relatively light weight lapping rings. The crystals were lapped on cast iron lapping rings to approximately their final thickness using 14.5 μ and 5 μ lapping compound obtained from the P. R. Hoffman Co. They were then polished using 5 μ or 2 μ diamond powder in a vehicle of olive oil or light petroleum oil on Pellon paper attached to aluminum lapping rings in the same machine. All gears, including the bakelite carrier gears, were changed for this polishing operation to prevent contamination from the previous lapping step. The polished crystals were optically clear except for some very small pits which were visible under a microscope.

Every sensor has three electrodes, each of which is evaporated separately after outgassing the sample for one hour at 150°C. To minimize the time required for these multiple evaporations, a bell jar vacuum system was set up with two separate tungsten evaporation filaments and with a sample outgassing oven which allowed the evaporation of an electrode both from above and below each filament simultaneously. This allowed as many as four electrodes to be evaporated for each pump-down and outgassing.

The evaporation filaments were 3 x 0.030" tungsten wire bent in the form of a horizontal loop with a diameter of 1.25". They were positioned approximately 2" above the sample and centered over it to insure uniform evaporation thickness and to "miss" the sample if any hot aluminum fell from the tungsten filament. Several pieces of #26 gauge pure aluminum wire, each 0.6" long, were wrapped symmetrically around the tungsten filament for each evaporation. It

was possible to obtain as many as twenty evaporation runs from a single tungsten filament before replacement. To obtain uniform evaporations from such a filament it was found helpful to outgas the tungsten filament initially and to then make one evaporation with no sample in place solely for the purpose of wetting the tungsten.

The first electrode to be put on each sample was the guard electrode which required two masks, a thin shoulder ring to define the outer edge of the guard electrode and to prevent electrical short-circuiting of the sensor by the evaporated film, and a carefully machined conical mask which defined the critical inner edge of the guard electrode. The conical mask was positioned at the center of the crystal by the split jig shown in Figure 2 and was spring loaded to improve its mechanical stability and thermal contact with the outgassing oven. The sample was wiped with a fine artist's brush to remove any dust particles, then indexing numbers approximately 0.040" high bent out of 0.003" copper wire and pressed flat were placed near the outer edge of the guard electrode and were positioned as desired with a fine sewing needle.

The bell jar was put in place and the vacuum system was pumped down to $\sim 1\mu$, at which time the outgassing oven was turned on and the evaporation filaments were heated to a dull red. The outgassing oven employed a radiant coil heater under a 4" x 7" plate of 0.090" aluminum. A thermocouple combined with a "Simplytrol" photocell meter were used to maintain the temperature at the center of this

Figure 2. Setup for evaporation of guarded electrode

- (a) Split jig
- (b) Conical mask
- (c) Shoulder ring
- (d) Indexing numbers
- (e) Sample

plate at 150°C after an initial warmup time of 30 min., which was slow enough that the crystals were not thermally shocked. After one hour at 150°C the pressure had usually fallen to $< 10^{-5}$ Torr and the mask and sample had reached thermal equilibrium.

Each tungsten evaporation filament was then heated individually until all of the aluminum had melted and uniformly wet the tungsten wire, at which time the temperature was increased at a fairly rapid rate until the aluminum had evaporated completely. Overlapping of the films from the two filaments was prevented by a shield placed between the two evaporation setups in such a way that each sample could not see any part of the wrong filament. When the evaporations were completed the oven was turned off and allowed to cool to $\approx 50^\circ\text{C}$. The cooldown time was adjusted to be ≈ 45 minutes by using copper strips to thermally sink the oven to the bell jar base plate. (These copper strips should not be too heavy or they would cause significant temperature gradients in the oven.)

After the oven had cooled to 50°C the bell jar was opened and the conical mask, shoulder ring, and indexing numbers were carefully removed from the sample to avoid scratching the rather soft aluminum surface. The sample was then inverted and gently placed on the washer-type mask shown in Figure 3 in preparation for the second evaporation.

The evaporation of the guarded electrode is more involved since in order to obtain a uniform guard gap it is necessary to position the sample on the washer-type mask so that the hole in the mask is concentric with the evaporated guard electrode within

Figure 3. Setup for evaporation of guarded electrode.

- (a) Pressure finger.
- (b) Stabilizer strip.
- (c) Sample with previously evaporated guard electrode.
- (d) Brass roller.
- (e) Spring (sewing needle).
- (f) Adjusting screw.
- (g) Washer-type mask

0.0002". (A 0.0002" offset with an average gap width of 0.0005" results in a minimum of 0.0003" and a maximum of 0.0007", more than a factor of two.) To allow this adjustment each washer-type mask had three spring-loaded adjusting screws to position the sample and allow for isotropic thermal expansion. The actual positioning was done using a 25 power microscope fitted with a displaced rotating stage to allow observation of the overlap of the brass mask at the guard gap radius. The final settings not only required that the sample be positioned correctly, so that the width of the brass strip as seen through the microscope was uniform as the stage was rotated, but also that the spring tension was adjusted to minimize backlash, as observed under the microscope when springing the sample first in one direction and then the other in a direction across the gap. With this setup it was possible to position the sample and check for acceptable backlash in 10-15 min., and the resulting failure rate (a short circuit between the guard and guarded electrodes) was only 10% for a gap width of 0.0005".

After positioning the sample on this washer-type mask the mask was inverted and placed under the evaporation filament, and the guarded electrode was evaporated in the same manner as the guard electrode. When the oven had cooled the sample was removed from the mask and checked for infinite electrical resistance across the guard gap and visually to observe the uniformity of the gap. If these tests were acceptable the opposite side of the sample was shielded with a shoulder ring and placed in the upper oven above the evaporation filament, and the high electrode was then evaporated as

before. This completes all preparation of the sensor itself, although the completed sensor must be mounted in some kind of sample holder to be useful as a three-terminal capacitor.

The sample holders which were used in the prototype apparatus are shown in Figure 4. Since it was desired to run more than one sample at a time the sample holders were in the form of brass cells which could be stacked as desired. These cells were grooved to form channels for the electrical connecting wires. Each brass cell contained a low and a high electrode cut from brass shim stock and attached to linen-base phenolic backing plates which were inserted into the cell. These electrodes were cut and formed in such a way that there were many points of contact between each electrode and the sensor, both to minimize electrical contact resistance and to evenly distribute the necessary contact force. A third electrode in the form of a serrated ring was used to insure electrical contact between the guard electrode and the cell, which was at ground potential. This electrode also acted as a shock absorber in case of sudden pressure changes. Short lengths of 36 gauge (7 x 44) teflon insulated wire were soldered to the low and high electrodes and were routed so that there was no leakage capacitance between the wires. These wires were then positioned in the grooved channels and connected to high pressure electrical feedthroughs in the plug of the pressure vessel and ultimately to BNC fittings at the top of this plug.

Figure 4. Pressure gauge sample holder.

- (a) Phenolic backing plate for low electrode.
- (b) Low electrode (0.0015" brass shim stock).
- (c) Serrated ring (0.0015" brass).
- (d) Sample.
- (e) High electrode (0.003" brass).
- (f) Backing plate for high electrode.
- (g) Grooved channels for electrical leads.
- (h) Stackable brass cell.