

Research Report 198
ELECTRICAL CONDUCTION IN ICE

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PREFACE

The experimental work reported herein was accomplished by Dr. Paul R. Camp, Physicist at Large, U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL); Walter Kiszénick of the Polytechnic Institute of Brooklyn, Expert, USA CRREL; and SP4 David A. Arnold, Research Division (James A. Bender, Chief), USA CRREL. This work was completed in the summer of 1964.

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SUMMARY

In an attempt to resolve the conflict existing in the literature as to the dc electrical conductivity of ice, an extensive series of measurements has been made. Since surface conduction is a possible cause of some of the confusion, both bulk conductivity and surface conductivity have been measured at both dc and audio-frequencies. Evidence was found for significant surface conductivity when slight contamination was present. In order to explain these results quantitatively, it is necessary to postulate a surface conduction region whose thickness varies with temperature.

Extrinsic bulk conductivity due to trace impurities has been found to play an important part also and probably accounts for some of the disagreement in the literature. Guard ring experiments show that, even for rather pure samples, the contamination is greater near the outside edge of the sample than in the center. Special efforts have been made to develop techniques which insure very high sample purity. These include purifying the water, cleaning and leaching the apparatus, growing the samples in the measuring cells so that no processing is required after preparation, and using special techniques for growing the samples themselves.

Using ice of the highest purity, both ac and dc conductivity measurements show that, for a fresh sample, the dc conductivity is nearly independent of temperature (possibly rising as $1/T$) down to temperatures at which the high frequency ac and dc conductivities are roughly equal. Below this temperature, the dc conductivity drops rapidly with decreasing temperature and the high frequency ac conductivity tends to level off. The results suggest that the high frequency conductivity is limited by two processes in parallel and that the dc conductivity is limited by the same two processes in series. Plateau values as low as 2×10^{-11} (ohm cm) $^{-1}$ have been found. This plateau disappears after the crystals have been annealed for a day at -5°C . The disappearance of the plateau with time may be the result of the diffusion of impurities in from the walls of the container. In this case the concentration of ions in ice and hence the dissociation constant must be much lower than has been commonly believed. On the other hand, the plateau may be a trapping phenomenon and the traps may anneal out with time.

The literature is surveyed and considerable experimental detail is included.

SYMBOLS

A	pre-exponential constant in Arrhenius equation having appropriate dimensions
a	pre-exponential constant in Arrhenius equation having appropriate dimensions
C	capacitance, $\mu\mu\text{f}$
C_j	concentration of ions of type j
D	diffusion coefficient (also symbol for D type Bjerrum defect)
E	activation energy in kcal/mole for process under discussion. Where confusion might arise subscripts are used, as E_r = activation energy for relaxation
E	(in App A) electric field strength
f_m	frequency of relaxation, ohms
G	conductance, ohms^{-1}
i	current; subscripts b, f, s, indicate bulk, fringing and surface respectively
J_s	saturation current
j	$\sqrt{-1}$
k	Boltzmann's constant
$K_{\text{H}_2\text{O}}$	Equilibrium constant
k_R	recombination rate constant
k_D	dissociation rate constant
l (or l)	length (also liter)
m	number of mobile ions per cm^3
m_s	number of mobile ions per cm^2 of surface
N_0	Avogadro's number
n	number of ionizable molecules per cm^3
n_s	number of ionizable molecules per cm^2 of surface
pdf	picofarad = 10^{-12} farad
q	charge per ion
R	gas constant
R	resistance
t	time (seconds unless units indicated)
Δ	displacement distance
δ	effective thickness of surface layer
ϵ	dielectric constant (dimensionless)

SYMBOLS (Cont'd)

ϵ_0	permittivity of free space (8.85×10^{-12} farad/meter)
ϵ^*	complex dielectric constant $\epsilon^* = \epsilon' + j\epsilon''$ ϵ' = real part ϵ'' = imaginary part
ϵ_∞	radio frequency dielectric constant
ϵ_s	static dielectric constant
ϵ_w	dielectric constant (real) for water
ϵ_i	energy to create an ion pair
ϵ_μ	energy barrier to mobility
ϵ_{eff}	effective dielectric constant
θ	constant having dimensions of temperature
λ	distance between crystal lattice sites
μ	mobility
μ^+	mobility of positive ions
μ^-	mobility of negative ions
μ^0	mobility of D defect
μ^L	mobility of L defect
ν	frequency of lattice vibrations and frequency of jumps between lattice sites
ρ	resistivity (ohm-cm)
σ	conductivity (ohm-cm) ⁻¹ ; subscripts a, b, s indicate apparent, bulk, and surface respectively
τ	relaxation time (sec)
ω	angular frequency (radians/sec)

ELECTRICAL CONDUCTION IN ICE

by

P. R. Camp, W. Kiszénick and D. A. Arnold

I. INTRODUCTION

The electrical conductivity of ice must be associated with the movement of charge. There are only four simple ways in which this can occur: by the motion of free, or nearly free, electrons or holes as in a semiconductor; by the passage of ions through the sample; by the reorientation of permanent dipole moments (water molecules); or by the induction of molecular or atomic polarization. The first two mechanisms might give rise to a continuous motion of charge and hence to a dc conductivity. The last two can give rise only to displacement current and hence to ac conductivity. This conductivity will be apparent only at frequencies of the order of, and larger than, the relaxation frequency of the polarization mechanisms. Thus the molecular and atomic polarizations, which have very short relaxation times, will be significant only at optical frequencies. These effects are about the same in both water and ice. The relaxation time for the reorientation of a molecular dipole is longer. In water it is of the order of 10^{-10} sec (Smythe, 1955) at 0C and decreases with increasing temperature. Thus the ac conductivity of water due to dipole rotation is small at frequencies below 10^9 cps. The dielectric constant ϵ , for frequencies less than 10^8 cps, is independent of frequency to within a few parts per thousand (Dorsey, 1940) and may be represented by the equation due to Wyman* where t is the temperature in °C.

$$\epsilon = 78.54 [1 - 0.00460(t - 25) + 0.0000088(t - 25)^2] \quad (1)$$

In ice the situation is quite different. The molecular rotation is hindered by the constraints of the lattice. Thus the characteristic orientational relaxation frequencies are in the audio-frequency range and dipole rotation gives rise to a fairly large ac conductivity at temperatures near the melting point (of the order of 1.4×10^{-7} (ohm cm) $^{-1}$ at -12C) for frequencies above the dispersion region. There is also the possibility of displacement current resulting from the translation of protons along oxygen-oxygen bonds. That is, under the influence of an electric field, a proton may jump from its equilibrium position as a part of one water molecule to another less stable position close to the other to which it is hydrogen bonded. Granicher et al. (1957) have given reasons for believing that this process occurs with a relaxation time much longer than 1 sec even at temperatures close to the melting point. Thus its resultant dispersion has not been measured. They have calculated a contribution of about 25 to the dielectric constant due to this process. Since for a simple Debye type dispersion the high frequency conductivity σ_D is given by

$$\sigma_D = \epsilon \epsilon_0 / \tau \quad (2)$$

where τ is the relaxation time and ϵ_0 is the permittivity of free space, a relaxation time of less than 1 sec implies an associated conductivity of less than 10^{-9} (ohm cm) $^{-1}$.

*Quoted by Smythe (1955, p. 86).

We have said that dc conductivity might arise from electron (or possibly hole) conduction or from ions. Granicher et al. (1957, p. 54) note that the intrinsic absorption band occurs at a wavelength of 1670\AA , which corresponds to a forbidden energy gap of 7.42 ev. This is so large as to preclude intrinsic electronic conduction. Thus, for pure ice, we are left with ionic conduction as the only mechanism which can cause appreciable dc conductivity.

It follows that for pure ice at radio frequencies and below, the processes of dipole rotation and ion (H^+ or OH^-) migration are responsible for the conductivity and dielectric constant. A general theory of ice as a conducting dielectric medium based on these processes has been developed by the group at the Eidg. Techn. Hochschule in Zurich and is outlined in Granicher et al. (1957) and Jaccard (1959). It is framed so as to include the effects of substitutional impurities (e.g., HF instead of H_2O) also. It predicts a general form of behavior with certain constants to be derived from experiment. These are frequency factors, dissociation constants, activation energies and intrinsic conductivities. Thus, although very carefully worked out and elegant in its symmetry, the theory leaves much to experiment.

The experimental situation for the ac properties is in fairly good shape, there being general agreement among different observers as to details of the Debye dispersion for pure ice as a function of temperature.* However, ac measurements on pure ice do not test the theory very rigorously because all they require is a theory which results in a Debye type dispersion. A further test is provided by experiments on "doped" ice, ice which contains substitutional impurities.†

However, impurities such as this introduce additional degrees of freedom into the theory in terms of new activation energies, and make its detailed corroboration difficult. One such impurity is HF, and the effect of HF concentration in the ac experiments is in accord with theory. The experimental situation for dc conductivity is much less satisfactory. As will be seen in the next section, there is little significant agreement among observers in different laboratories as to the conductivity of "pure" ice or even as to its temperature dependence. Activation energies for conduction ranging from 7 to 24 kcal/mole have been reported. The data seem to divide naturally into three groups: about 7, 13 and 24 kcal/mole respectively. Experiments with doped ice are in better agreement and give rise to low values of activation energy, a fact which suggests that the low values are the results of impurities.

Because responsible experimenters in different laboratories find such widely different activation energies for conduction it is evident that they are really measuring different processes. It is most natural to assume that some are measuring an impurity conduction and that this may account for the low values of activation energy. Since impurity conduction must be considered as in parallel with the intrinsic conduction of pure ice, it can be significant only if the activation energy is smaller than that for pure ice (at least unless one goes to rather complicated models). But this interpretation still leaves two very different processes to be resolved. It occurred to us that one of these processes might be surface conduction, leaving true bulk conduction as the other.

*See for example Auty and Cole (1952), Humbel, Jona and Scherrer (1953) and Camp (1963).

†See Granicher et al. (1957), Brill and Camp (1961), Kakiuchi and Shishikura (1962), and Brill et al. (1957) for experimental work and Jaccard (1959) for further discussion.

These considerations have led us to undertake the fairly extensive series of experiments on both bulk and surface conductivity which are reported here. Because the lack of experimental detail in the published literature proved a handicap to us both in our experiments and in our attempts to interpret the literature, we give, in what follows, a fairly complete account of our major experiments and the difficulties we encountered, together with the occasional pitfalls and frustrations we met along the way.

II. BACKGROUND

One of the earliest measurements of the conductivity of ice was that made by Ayrton and Perry in 1877. It is now probably of historical interest only. The ice sample was prepared by freezing distilled water between copper plates. The resistance was determined by measuring the current through the ice for a given applied voltage. It seems clear from their data that polarization and impurities played important roles in their measurements.

In 1912 Johnstone improved on these measurements by using platinum electrodes, pure water and a four-probe technique to sidestep polarization at the electrodes. His measurements were made on ice frozen in a glass U tube from water having a resistivity of about 1.4×10^6 ohm-cm. His data were somewhat erratic and sketchily reported (e.g., the data in his graphs do not seem to agree with those given in his tables). Yet he is often quoted. This is somewhat odd inasmuch as, depending on how one uses his data, one can find activation energies ranging from 19 to 33 kcal/mole. The conductivity he obtained at -10°C was about 10^{-9} (ohm cm) $^{-1}$, a factor of two smaller than that of Ayrton and Perry.

In 1951 Bjerrum proposed the existence in ice of a new type of point defect, the orientational defect, to explain the electrical properties of ice. These are structural defects arising from the misorientation of water molecules and appear in pairs as the absence of a hydrogen bond where one should be, the L defect, and a double hydrogen bond where there should be only one, the D defect. Bjerrum's idea, which has been widely accepted, was that these defects occur in thermal equilibrium with the ice lattice and make possible the rotation of molecules within the lattice. This rotation gives rise to the low frequency dielectric constant. It must also occur in concert with ion migration to permit the flow of a dc current.

Bjerrum used Johnstone's values for the conductivity of pure ice as evidence that the ion concentration in ice is of the same order as it is in water, * basing this on the assumption that proton jumps between ions and H_2O molecules occur in ice with almost the same frequency as they do in water. This assumption is no longer believed to be valid (cf., Eigen and DeMaeyer, 1956). Extrapolating Johnstone's data to 0°C he obtained a dc conductivity for ice of 4×10^{-9} (ohm cm) $^{-1}$ and a (presumably faulty) molecular concentration of ions of 1.3×10^{-8} .

*Johnstone's value for conductivity at -1°C is anomalously high, even higher than that of water. This point is disregarded in the extrapolation. Bjerrum computes the conductivity of water (0°C) from known ion mobilities and an ionization constant of 1.19×10^{-15} . He finds it to be 1.2×10^{-8} (ohm cm) $^{-1}$.

Combining the Einstein equation for diffusion and the Nernst-Einstein equation relating the diffusion coefficient D to the mobility μ through the charge e ,

$$D = \bar{\Delta}^2 / 6 \tau = \mu kT/e, \quad (3)$$

Bjerrum was able to express the average time τ for an ion to be displaced from one molecule to an adjacent one in terms of the mean square displacement distance $\bar{\Delta}^2$ and the mobility, and hence the conductivity. T is the Kelvin temperature and k is Boltzmann's constant.

Using the molecular conductivities obtained from his assumptions about the relation between proton jumps in ice and in water, he calculated a rate of proton jump displacements of 4.15×10^{11} /sec for the H_3O^+ ion and 1.6×10^{11} /sec for the OH^- ion. From the ion concentration calculated above, he estimated the rate of proton jumps per H_2O molecule to be 152/sec. Although the argument is useful, the premise and with it all the conclusions are in doubt. Thus much depends on the true value for the dc conductivity of ice.

From the data for the electrical conductivity in dilute aqueous solutions of the ions H_3O^+ , K^+ , HO^- , and Cl^- , Bjerrum extracted the molar conductivities due to proton jumps in water and their activation energies. Using these, and breaking the dissociation energy of water into two parts, that due to the proton jump and that due to the separation of the ions, he developed two theoretical expressions for the activation energy for conduction in ice. One, based on a dielectric constant of 88 for ice, is 9.95 kcal/mole. The other, based on a dielectric constant of 5.9 (the radio frequency value), is 19.75 kcal/mole in (forced) agreement with the data he cites from Johnstone. Use of such a value for the dielectric constant requires that, once formed, the ion pair separates in the order of 10^{-5} sec.

It is interesting to note his remark to the effect that because the ions must move through ice by proton jumps only, "... impurities do not have the same large effect on the conductivity of ice as they have on water. It is therefore easier to determine experimentally the conductivity of pure ice than of pure water." Apparently he never tried to measure it himself.

Conductivity measurements made by Bradley (1957) in 1956 over a rather limited temperature range (-2 to -24C) give an activation energy of 12.3 kcal/mole and a pre-exponential term of 23.4 (ohm cm) $^{-1}$ for the region below -6C. His data converge with those of Johnstone at high temperatures (above -10C) but diverge at lower temperatures. The measurements were made using a two-electrode technique in a silica and polyethylene cell. The water had an initial conductivity of 2×10^{-6} (ohm cm) $^{-1}$ at 25C and was repeatedly frozen and melted under vacuum in the cell in order to remove the air. The electrodes were palladium foil welded onto platinum, and the ice, which was frozen up from the bottom of the cell, was annealed for days before measurements were begun. Some polarization was clearly encountered because the current was measured as a function of time and extrapolated to zero time. The data for water were extrapolated from values quoted by Dorsey.

In 1956, Siksna (1957) at Uppsala measured the electrical conductivity of large single crystal blocks of ice (typical dimension perhaps 5 cm). These were cut and polished by hand and mounted between electrodes of unspecified material. The resistivity measurements were made by discharging a capacitor of known size charged to 135 volts through the ice cell and measuring the time constant of the discharge. It is clear from his paper that polarization played an important part in his measurements and it is not surprising that neither his values nor their variation with temperature were reproducible. At -10C, he found conductivities ranging from 5×10^{-10} to 1.2×10^{-8} (ohm cm) $^{-1}$. He did not analyze his temperature dependence in terms of activation energy, but the values of conductivity are such as to indicate activation energies in the range of 12.5 to 40 kcal/mole. As Siksna

indicates in his discussion, these measurements tell us little about the properties of pure ice but suggest some of the problems in connection with their measurement.

Granicher et al. (1957) have developed a theory to describe the electrical properties of ice, both ac and dc, in terms of four kinds of point defects, the D and L defects of Bjerrum and positive and negative ions (H_3O^+ and OH^-). This has been expanded and treated in detail by Jaccard (1959). It follows from the theory that the dielectric constant, dispersion frequencies, and conductivity of ice will depend in a prescribed way principally on the abundance and mobilities of these four defects. However, it remains for experiment to provide these numbers.

Measurements of the ac properties (Granicher et al., 1957; and others) as interpreted by this theory lead to the conclusion that they are determined largely by the Bjerrum defects. Experiments on ice doped with HF to increase the concentration of L defects in a known way (Jaccard, 1959) lead to a value for the mobility of the L defect ($\mu^L = 2 \times 10^{-4} \text{ cm}^2/\text{v-sec}$ at -10C) and a value for the D defect less than or equal to this. From ac measurements on pure ice, one may then estimate the concentration of D and L defects (n^D and n^L) with the result that

$$n^D = n^L = 3 \times 10^{23} e^{-E_{DL}/2RT} \text{ cm}^{-3} \quad (4)$$

where

$$E_{DL}/2 = 0.34 \text{ ev} = 7.9 \text{ kcal/mole.} \quad (5)$$

It is also evident that the concentration of ions in pure ice must be much smaller than that of Bjerrum defects.

An additional consequence of the theory is that the dc conductivity of ice will be limited by whichever is in the minority, ions or Bjerrum defects. Thus, to explore the properties of the ions it is necessary to measure the dc conductivity. This has also been done by Granicher et al. Starting with water of conductivity 10^{-6} to $10^{-7} \text{ (ohm cm)}^{-1}$, ice samples were prepared. Electrodes of Au, Pt or Ag foil were frozen onto their surfaces. It was found that completely reproducible results could not be obtained and that the currents measured for a constant applied voltage were not time independent. However, when gold electrodes were applied by evaporation in a vacuum at liquid nitrogen temperatures, time independent currents could be obtained. Measurements on samples prepared in this way gave a dc conductivity at -10C of 10^{-8} to $10^{-9} \text{ (ohm cm)}^{-1}$ and an activation energy of 0.6 ev (14 kcal/mole). Jaccard also quotes experiments of this kind for an applied field of 250 volts/cm which gave a -10C conductivity of $10^{-9} \text{ (ohm cm)}^{-1}$ and an activation energy of 0.61 ev. It is not clear whether or not this represents an additional experiment.

Granicher et al. also report experiments in which a slab of pure ice was sandwiched between two layers of HF-doped ice. Pt or Au electrodes were then frozen to the doped layers. This arrangement gave ohmic contact from 125 K to 250 K and an activation energy of 0.32 ev (7.5 kcal/mole) with a pre-exponential of about 4 (ohm cm)^{-1} . The corresponding conductivity at -10C would be about $3 \times 10^{-6} \text{ (ohm cm)}^{-1}$. The explanation offered is that H_3O^+ ions and L defects diffuse rapidly into the pure ice from the doped sections and thereby increase the density of charge carriers in proportion to their concentration in the doped layers. This interpretation raises the question of what happens in any piece of ice, which must be bounded by surfaces which are sources or sinks for the different defects.

Eigen and DeMaeyer (1958) have attempted to measure the ionic concentration C_j and the ion mobilities μ^+ and μ^- in ice by other means and hence to deduce the conductivity. They used several different experiments.

The dissociation equilibrium of water ($H^+ + OH^- \xrightleftharpoons[k_D]{k_R} H_2O$, in which $k_R =$ recombination rate constant and $k_D =$ dissociation rate constant) is altered in strong electric fields. From the magnitude of this change, a value of the effective dielectric constant involved in dissociation, ϵ_{eff} , may be deduced. The relaxation time when the field is removed, τ_c , is given by $\tau_c = 1/(2k_R C_j)$ where C_j is the concentration of ions. This can be measured experimentally. Thus if k_R can be found, C_j may be determined. Another effect of high fields is that ions are swept out as fast as they are formed and thus a measurement of the saturation current J_s leads to a value of the dissociation constant which is related to k_R through the equilibrium constant K_{H_2O}

$$K_{H_2O} = C_j^2 / C_{H_2O} = k_D / k_R \quad (6)$$

Thus

$$C_j = 2k_D \tau_c C_{H_2O} \quad (7)$$

Each member on the right can be inferred from experiment.

From their measurements on water and ice, Eigen and De Maeyer have found

$$C_j (\text{ice } -10C) = (3 \text{ to } 15) \times 10^{-11} \text{ mole/l}$$

which gives an equilibrium constant

$$K_{(H_2O)} (\text{ice } -10C) = (2 \text{ to } 40) \times 10^{-23} \text{ mole/l}$$

as contrasted with that for water

$$K_{H_2O} (\text{water } 25C) = 1.821 \times 10^{-16} \text{ mole/l.}$$

From the detailed behavior of the saturation current as a function of field, they were able to estimate also the product $C_j \sqrt{\mu^+ \mu^-}$ where μ^+ and μ^- are respectively the mobilities of the positive and negative ions. Another relation gives k_R as a function of $(\mu^+ + \mu^-) / \epsilon_{eff}$. Thus C_j , μ^+ and μ^- may be determined independently of the conductivity σ .

$$\sigma = n_j q (\mu^+ + \mu^-), \quad n_j = \frac{C_j N_0}{1000} = \text{ions/cm}^3 \quad (8)$$

where q is the ionic charge. The values so obtained lead to conductivities of about $(3 \text{ to } 70) \times 10^{-10} (\text{ohm cm})^{-1}$ for ice at $-10C$, which effectively bracket those found experimentally by Johnstone, Bradley, and others and would thus tend to confirm them. However, it is not clear to us that the measurements of Eigen and De Maeyer are intrinsically any less dependent on impurities, surface and electrode effects, etc., than are the measurements of conductivity. Put another way, the question

is this: Do both types of experiment measure effectively the same things (and consequently give similar results), and if so are these the properties of pure ice? Certainly if the results of several different observers measuring substantially different effects happen to more or less intersect at -10°C it is not surprising if another measurement arrived at by a more circuitous route gives a value also in this range. It would be useful to find out if Eigen and De Maeyer's numbers would change appropriately for ice doped with a known impurity.

In the meantime, it seems evident from the variety of activation energies reported that different observers are measuring different things. One cannot accept with confidence the value of σ at -10°C as being that of pure ice simply because the various curves intersect at about this temperature.

More recently (1962), Heinmets and Blum (1963) measured the conductivity of ice under what they believed to be conditions of high purity (demineralized distilled water passed through a millipore filter).^{*} The cell was apparently Pyrex, although its material is not specified, and it also contained some cellulose acetate.[†] In order to remove the dissolved air, the water in the cell was repeatedly frozen and melted under vacuum. The cell was then refrozen, opened and a solution of HCl in glycerine was poured into each end to form electrodes. Electrical contact was established by immersing platinum plates in this liquid. In this way apparently they were able to produce nearly time independent currents (although they do mention some trouble in obtaining "stable conductivity values").

With this apparatus (in contrast to the measurements of Granicher *et al.* who found a threshold potential of 1 volt in their sandwich electrode experiments) Heinmets and Blum found no evidence for a potential threshold down to 20 mv applied potential. Their early experiments, which they dismiss as unsatisfactory for one reason or another, gave activation energy values of the order of 15 to 19 kcal/mole. The last two, in which they voice the greatest confidence, gave values of about 24.2 kcal/mole and a conductivity at -10°C of 1.6×10^{-9} (ohm cm)⁻¹. Their temperature range was small, -3 to -20°C , and above -7°C there was a sudden drop in conductivity. This anomaly is in the opposite direction to that reported by Johnstone and Bradley in the same temperature range.

Eighty-eight years have now elapsed since the measurements of Ayrton and Perry. Yet the question of the dc conductivity of pure ice and hence of its mechanism and of the ionic concentration remains unanswered.

III. SURFACE EXPERIMENTS

In order to test the surface conductance hypothesis several different kinds of experiments were performed. It was recognized at the outset that it would be extremely difficult to measure the properties of uncontaminated ice surfaces unless ice cleaned itself naturally by sublimation. However, since the purpose of these experiments was to find out whether or not surface conductance was important under more or less normal experimental conditions, we made the measurements in air, being careful not to contaminate the surface but without exercising the kind of experimental care which is required for measurements on

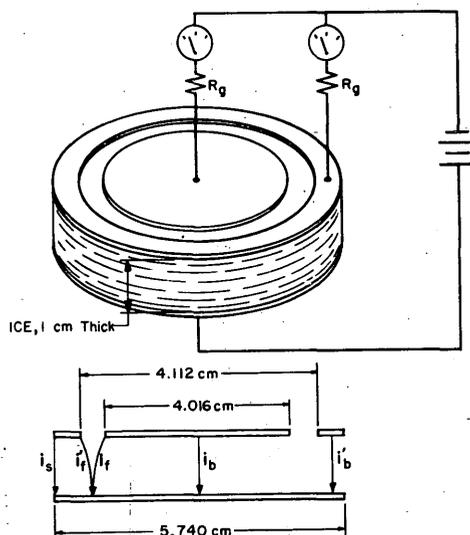
^{*}We have been unable to maintain the low conductivity of our best water when it is passed through a millipore filter. Heinmets and Blum do not report the conductivity of their water.

[†]Impurities may leach out of both of these materials.

clean surfaces. Because at the time we had no better water, our first experiments were done with samples grown from demineralized distilled water having a room temperature resistivity of 2×10^6 ohm-cm. Since these early experiments seemed to indicate surface currents large compared to the bulk, there was no reason to obtain purer water until this thesis had been explored.

Guarded ring measurements

The first experiment was a guarded ring measurement (Fig. 1) in which the guard ring and center disk were of equal area. In this way, for the same potential difference, the bulk current through both zones should be the same. The current through the center disk can be considered as comprising two terms, the bulk current i_b due to bulk conductance and a fringing current i_f due to bulk conductance in the region between the disk and the ring. The ring current comprises three terms: bulk current i_b' , fringing current i_f' and a surface current i_s . Because of the geometry, $i_b = i_b'$ and $i_f = i_f'$. Therefore the difference between the ring current and the disk current should be i_s .



Sample 1 - 1.06 cm	Sample 7 - 0.77 cm
Sample 2 - 1.16 cm	Sample 8 - 0.77 cm
Sample 3 - 0.78 cm	Sample 9 - 1.09 cm
Sample 4 - 1.01 cm	Sample 10 - 1.08 cm
Sample 5 - 0.83 cm	Sample 11 - 1.05 cm
Sample 6 - 1.25 cm	Sample 12 - 1.05 cm
	Sample 13 - 0.93 cm

Figure 1. Guarded ring apparatus for separating bulk and surface effects.

This simple scheme has several drawbacks. For example, if there is electrode polarization, the currents will not indicate the true conductance. Moreover, unless the ammeter resistance R_g can be kept small with respect to the sample resistance, one instrument shunts the other through the sample thereby

distorting the measurements. Nevertheless, it seemed a useful experiment to give us an order-of-magnitude estimate of surface current. Accordingly, the apparatus of Figure 1 was constructed and used to study several samples of pure polycrystalline ice. The ice was grown from 2×10^6 ohm-cm water in a Lucite tube having just the diameter of the apparatus. It was then partially extruded from the tube, faced off and frozen to one plate. Then a section of the proper length was cut off, faced and mounted in a jig of the same tubing so that the other plate could be frozen on in the proper register. A voltage of $67 \frac{1}{2}$ v was applied to the sample and the resulting currents were measured using Keithley Model 200 electrometers equipped with the Model 2008 decade shunt.

Our measurements showed a much larger current in the ring circuit than that for the center disk. At -10°C the ratio of these currents was typically a factor of ten. Moreover, the temperature dependence of the ring current was substantially greater than that of the disk current. The difference from sample to sample was great but we attributed this to the polarization and shunting mentioned above and interpreted our results as an indication of large surface currents. It will be shown that we now believe this to have been a partly mistaken inference and our original measurements worthless. Therefore we have not included these data.

Slim rod 4-probe measurements

Believing that we had established the existence of large surface currents by means of the guarded ring experiment it remained to perform an experiment which avoided the difficulties already mentioned and thus obtain accurate measurements. Since the apparent surface currents were large compared to the bulk current even for a 1 in. diam sample, it followed that by using a sample in the form of a slender rod we could make the bulk current entirely negligible and thus use a standard four-probe technique to measure surface current.

The second experiment was such a four-probe measurement made on a series of polycrystalline ice cylinders of $\frac{1}{8}$ in. diam prepared by freezing 2×10^6 ohm-cm water in clean Pyrex tubes and then extruding the ice. The current electrodes were platinum wire loops 1 cm apart near the middle of the rod. Current was measured with a Keithley Model 200 electrometer with the Model 2008 decade shunt. Voltage was measured with a second Model 200 electrometer not shunted (input resistance greater than 10^{14} ohms), well insulated from the ground and electrostatically shielded. The use of polycrystalline ice in all of this work was justified on the grounds that the surface is such a discontinuity in the ice lattice that a few regions of slight mismatch below the surface could affect its properties only slightly.

The data shown in Figure 2 are typical of the measurements made with this apparatus. The two curves give the dependence of the surface conductivity in ohms^{-1} (which by virtue of the geometry is numerically equal to the conductance in ohms^{-1}) as a function of the reciprocal of the absolute temperature for the same sample, 10 days having elapsed between measurements a and b.

Several measurements taken in the intervening period all fall between these extremes, showing a general trend for the conductance to decrease slightly with time. The experimental points fall very nicely on straight lines from whose slopes an apparent activation energy for conduction, E , can be derived. The results of 11 different temperature runs on 2 different samples gave $E = 19.25 \pm 0.25$ kcal/mole. The average conductance at -10°C was $(3.3 \pm .5) \times 10^{-8}$ ohm^{-1} . If bulk current can be neglected, then, for the particular dimensions used here, the conductance is equal to the surface conductivity.

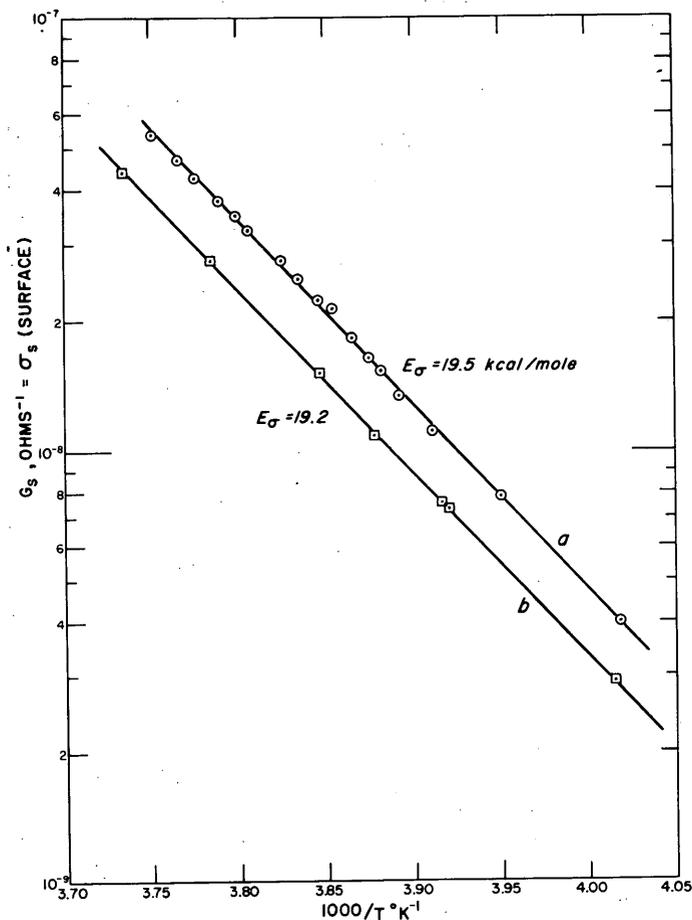


Figure 2. Conductance (ohms)⁻¹ vs 1000/T °K⁻¹ for slim rod experiments in air. Data of line b were taken 10 days after those of line a.

The slow decrease in conductance with time suggested that there was a gradual cleansing or poisoning of the surface depending on the point of view one took as to the nature of the conductance. To explore this matter, the atmosphere of one experiment was changed from air to CO₂. There was no measurable change in conductance or activation energy. In another experiment, the sample was immersed in kerosene; again there was no apparent change. At the time, these two experiments were interpreted to mean that the surface was already well contaminated before the experiments in air even though we had tried to avoid contamination. This contamination could have been simply a matter of absorbed gases. The reproducibility and stability of the samples made a good case for this interpretation. Nearly unavoidable surface contamination of this kind is consistent with the hypothesis that the high activation energies reported by some observers were a consequence of surface conductance. More will be said shortly about the implications of the actual numbers.

Large rod four-probe measurements

As a further test of the surface current hypothesis, two experiments were done with larger rods (diameter 2.8 cm and voltage probes 2.2 cm apart). The purpose

of these experiments was to show the transition from predominantly surface current at high temperatures to predominantly bulk current at low temperatures. Since these two currents must be measured in parallel and since the surface current seemed to have a much stronger temperature dependence as measured by the guard ring experiments than did the bulk current, it followed that the bulk current must be dominant at low temperatures. Since dc measurements at low temperatures are very difficult due to the high resistances involved, it was desirable to use a large enough sample so that the transition could be expected at a reasonable temperature.

The first sample was measured down to -31.5°C and behaved in a manner similar to that of the small rod except that the slope of the conductance vs $1/T^{\circ}\text{K}$ plot did not seem to be stable with time. Two different values of activation energy were obtained, 19 kcal/mole and 22 kcal/mole. Since this sample contained bubbles it was discarded and a new clear polycrystalline sample was prepared. Measurements on this sample were carried down to -68°C . The data are shown in Figure 3. It can be seen that the curve has the general features expected, a steep slope (21.6 kcal/mole) at high temperatures giving way to a smaller slope at low temperatures (13 kcal/mole). The crossover comes in the vicinity of -30°C . At -60°C there is a discontinuity in the curve but the same slope is retained. The reason for this discontinuity is not known. It may have been the result of thermal cracking although none was observed, or it may have been a systematic error in temperature measurement. (On the basis of later experience, we believe that true temperature equilibrium may not have been obtained in these measurements and that consequently the temperature of the sample was higher than the measured temperature of the environment.) The dependence of sample current on applied voltage at -10°C was measured and found to be almost linear up to 70 v. However, there appeared to be a residual potential of about 1.5 v across the current terminals, which were aluminum. Presumably this was a polarization potential resulting from the previous measurements. The relation between the current and the potential at the voltage electrodes was strictly linear and the residual voltage was less than 0.02 v.

A second measurement 5 days later on this same sample was disappointing. The data were erratic at about -30°C and again at -40°C and the steep initial slope did not materialize. Suspecting that part of the difficulty might be due to frost forming on the surface, we made current measurements with the sample deliberately frosted and again as it was clearing. The effect of the frost was to decrease the current by a factor of three or more. This fact also implies a large surface contribution to the total current. Further measurements on this sample failed to show the pronounced transition noted in Figure 3. The reason is not clear. However, it should be pointed out that the region below -30°C is a difficult one in which to make good measurements. Thermal cracks can develop because the ice becomes brittle, frost forms, the currents being measured become very small so that the measurements become highly susceptible to distortion by stray currents and polarization, and the time constants of the system become very large.

Guard ring ac measurements

If there is a large surface contribution to the dc conductance, it would be interesting and useful to study the ac properties as well. This can be done conveniently using the guard ring technique already described. For ac measurements electrode polarization is a problem only at very low frequencies and it is therefore unnecessary to use a four-probe technique. Since the guard ring experiment is a difference technique, it is possible in principle to cancel the bulk contribution entirely. The extent to which this can be done in practice depends primarily on the accuracy with which the sample dimensions can be controlled. A slim rod experiment has the disadvantage that, as the frequency increases, the bulk conductance

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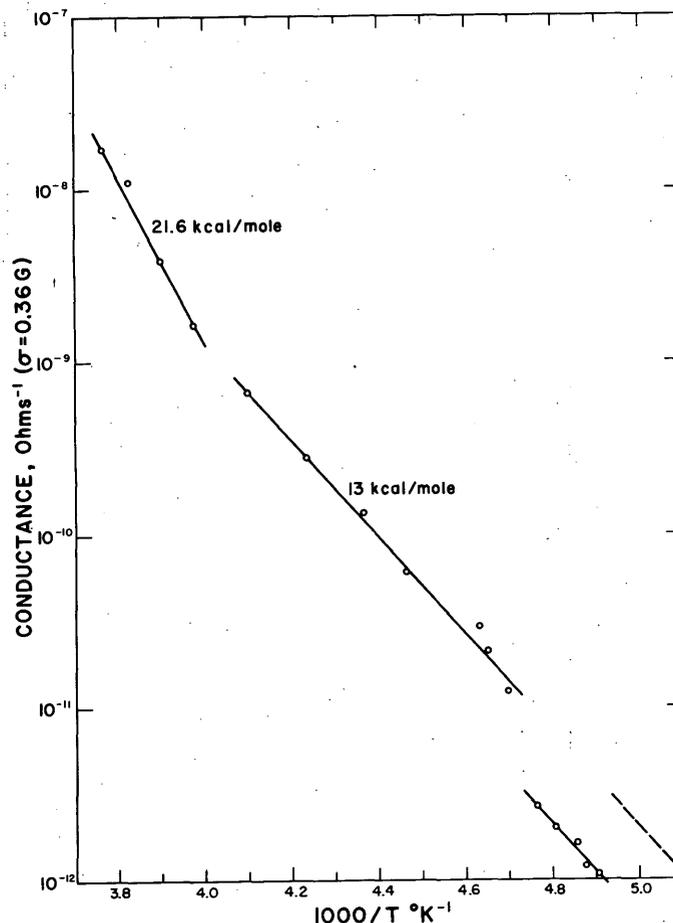


Figure 3. Conductance (ohms^{-1}) vs $1000/T$ ($^{\circ}\text{K}^{-1}$) of a large four-probe sample in air.

increases and at some point may become the dominant factor. Also fringing effects become troublesome.

An extensive series of guarded ring ac measurements was made using a General Radio Type 1615A capacitance bridge with a General Radio Type 1232A tuned null detector. This bridge is designed specially for three-terminal applications. The measurements were made as shown in Figure 4. First the standard guarded circuit arrangement was used to measure the bulk properties. Then the guard and disc connections were interchanged and the outer ring (bulk plus surface) properties were measured. Because the second arrangement does not prevent a slight fringing flux in the air surrounding the sample it can be expected to include a shunt capacitance of the order of 1 picofarad (pfd) due to fringing. The frequency range covered was 20 to 20,000 cps.

The first measurements were made using brass electrodes and polycrystalline samples. Later experiments included both polycrystalline and single crystal samples and platinum electrodes were used with one sample. All samples were prepared from demineralized distilled water having an initial resistivity of about 2×10^6 ohm-cm. Their dimensions are given in Figure 1.

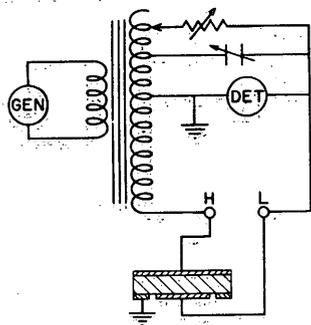


Figure 4. Simplified schematic diagram of the bridge circuit for ac measurements.

Nine physically separate samples were prepared and measured. Several of these then were modified (as will be explained) and remeasured, making a total of 13 samples. The first 10 were polycrystalline samples prepared as follows: a Lucite tube having the same inside diameter as our test cell was filled with demineralized distilled water which had been boiled to remove dissolved gases. The tube was filled hot and sealed. It was then placed on a cold plate in a freezer so that ice froze slowly up from the bottom. For samples 1 through 6, the ice was carefully extruded from the tube until a suitable region was reached. It was cut on a band saw, faced, and frozen onto one plate of our assembly. It was then extruded 1 cm further, cut again and frozen onto the other plate. This process was accomplished with the aid of a plastic sleeve for centering both plates on the sample.

To lessen the chance for contamination, the next four sections were cut without extruding the specimen from the tube. This destroyed the tube but left the sample encased in a Lucite jacket. The faces of the sample were then trimmed and the electrodes were frozen to it much as before. Measurements were made first with this plastic ring in place (samples 7, 9, 11 and 13). The ring was then removed by gently warming it and sliding it off over the electrodes and the measurements were repeated (samples 8, 10 and 12). It was clear from comparisons of the data that no change could be ascribed to the Lucite ring. Therefore, since it afforded protection to the sample, it was not removed from single crystal sample 13.

Samples 11, 12 and 13 were adjacent sections of a single crystal grown in a similar tube from similar water. However, in this case, the water was cooled and the gases were expelled by sealing the system and evacuating it to the vapor pressure of the water. Pumping with occasional shaking was continued until bubbles ceased to appear (about half an hour). Then the system was opened and seeded at the bottom with a single crystal seed. It was again evacuated and sealed and the tube was lowered seed end first into a cold bath at -27°C . The rate of lowering, and therefore the rate of growth of the crystal, was 3 mm/hr. The single crystal was sectioned and mounted in just the same manner as were polycrystalline samples 7-10.

Equivalent parallel conductance and capacitance for both bulk and bulk plus surface were measured as function of frequency in the range 20 - 20,000 cps for a number of different temperatures between 0°C and -30°C . Representative data are given in Figures 5-17. Figure 5 shows the behavior of sample 5 at -12.7°C which is typical of the early polycrystalline samples. This may be compared with Figure 12, a -12.0°C measurement of single crystal sample 12. When allowance is made for the fact that sample 12 is about 12% thicker than sample 5, the data for the two samples are in fair agreement, indicating at most a minor effect due to grain boundaries. We believe that the technique of preparing and mounting sample 12 was superior to that used for sample 5. Therefore the larger low-frequency conductance and capacitance of sample 5 is attributed in part to impurities. Sample 10, which was also polycrystalline, having fewer and larger crystallites than sample 5, also shows similar features (compare Figure 6 for sample 10 at -11.6°C with Figure 12 for sample 12, single crystal at -12.0°C). We are concerned here only with the bulk (center electrode) behavior. By virtue of

the fact that the crystallites of sample 10 are larger than those of sample 5 we would expect any grain boundary contribution in 10 to be smaller than that in 5. Thus we do not attribute most of the behavior of 5 and 10 to grain boundaries. However, on the basis of these experiments, we cannot exclude the possibility of some grain boundary contribution. As will be seen in Section V, subsequent experiments with very much purer materials lead us to believe that, for very pure samples, grain boundary effects are small.

Figures 7-13 show data for samples 11 and 12. These are measurements made on a single crystal using brass electrodes, first with the Lucite jacket in place (11) and then with it removed (12). Comparison of these curves shows that the Lucite ring has no measurable effect.

Figures 14 and 17 show the behavior of a single crystal sample (13) cut from the same bar as sample 12 and adjacent to it. This sample was measured in a test cell identical to that used before except that the electrodes were platinum plated. The data are very similar. A slight tendency can be seen for the brass electrode capacitance values to rise at the lowest frequency. This is absent in the platinum electrode measurements and we interpret it as a sign of electrode polarization for sample 11. An even more striking difference is seen between samples 5 and 10 (relatively impure with brass electrodes) and sample 11 (relatively pure with brass electrodes). Thus electrode polarization seems to be associated also with sample contamination.

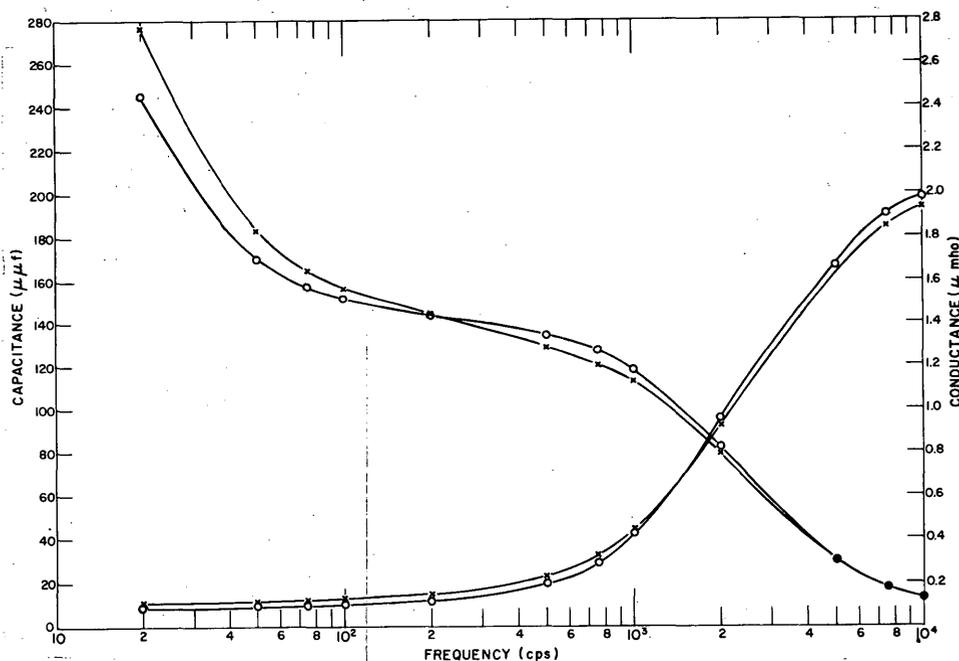


Figure 5. Sample 5, -12.7°C (polycrystalline, brass electrodes).

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode), 2×10^6 ohm-cm water.

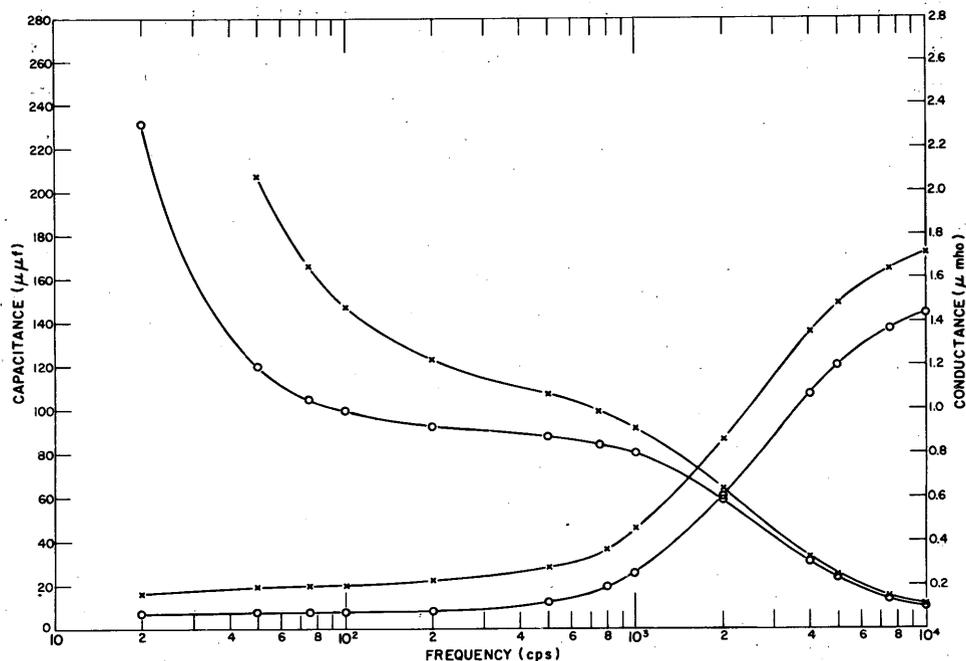


Figure 6. Sample 10, -11.6°C (polycrystalline, brass electrodes but with larger crystallites than sample 5).

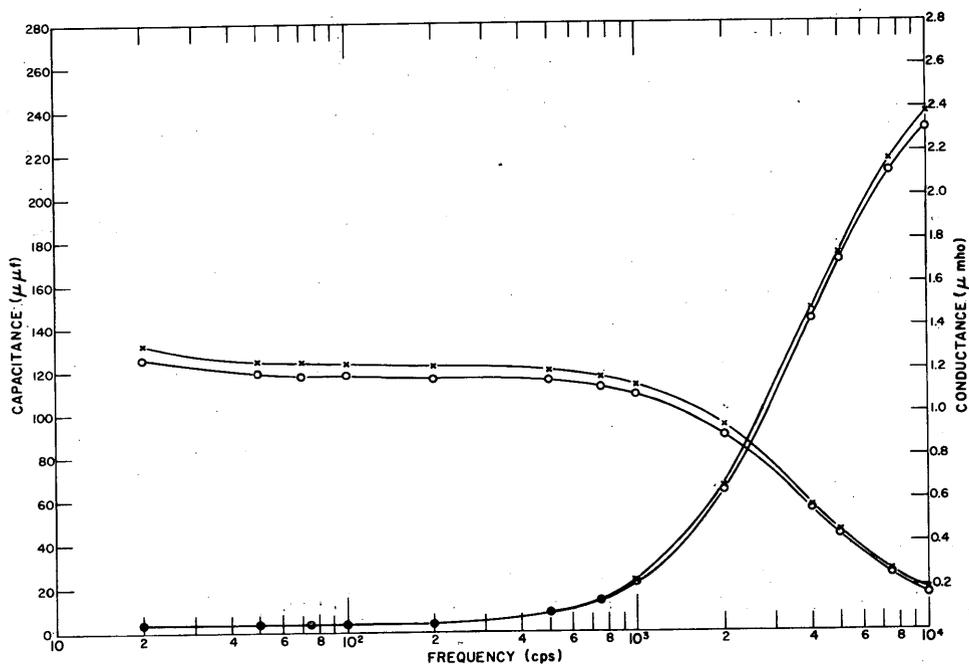


Figure 7. Sample 11, -8.0°C (single crystal, brass electrodes, with Lucite jacket).

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

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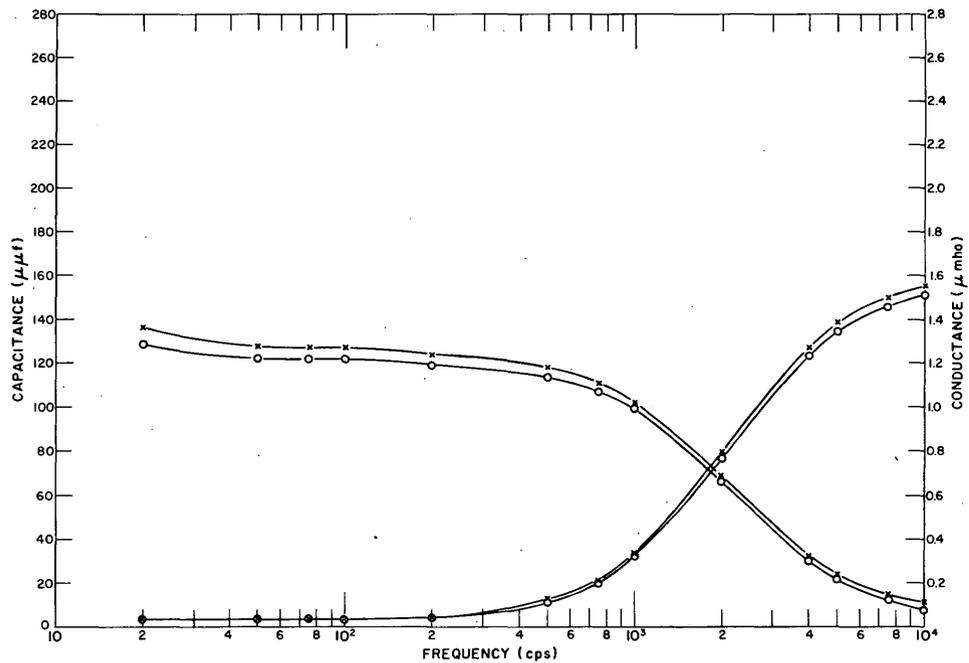


Figure 8. Sample 11, -12.8C.

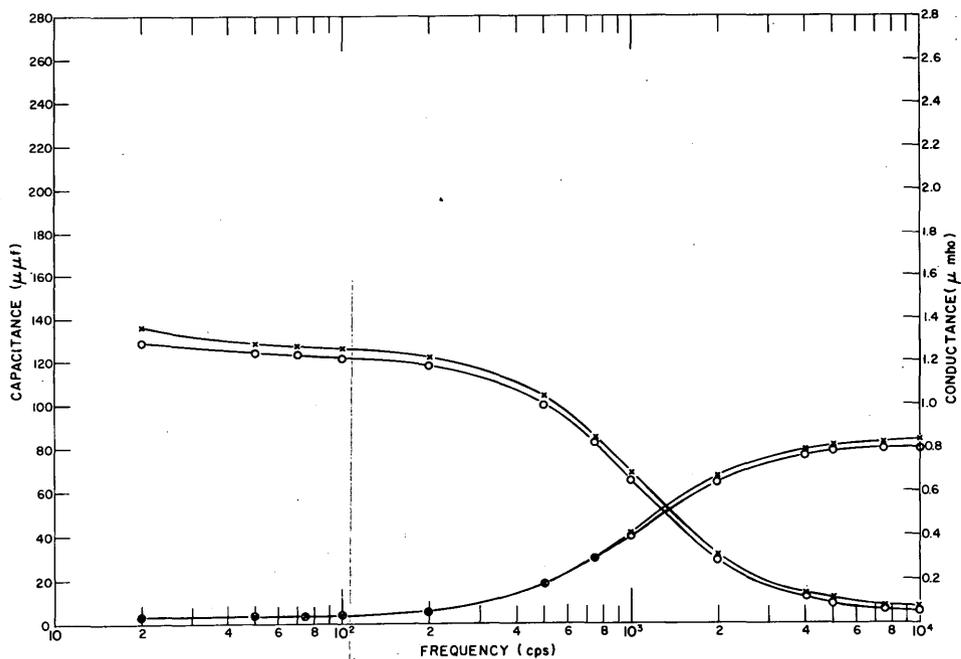


Figure 9. Sample 11, -19.5C.

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

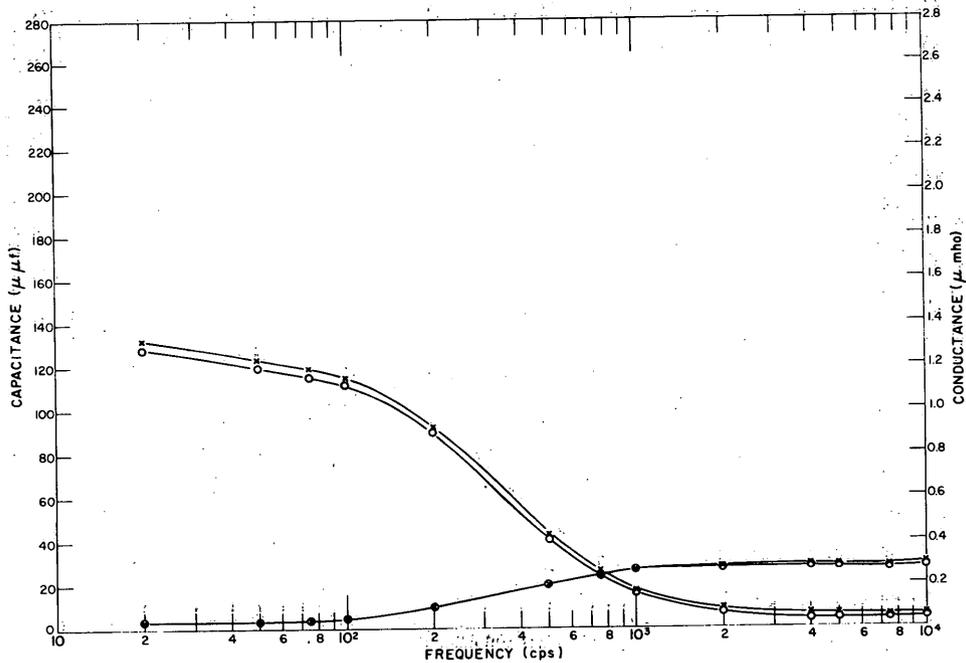


Figure 10. Sample 11; -30°C.

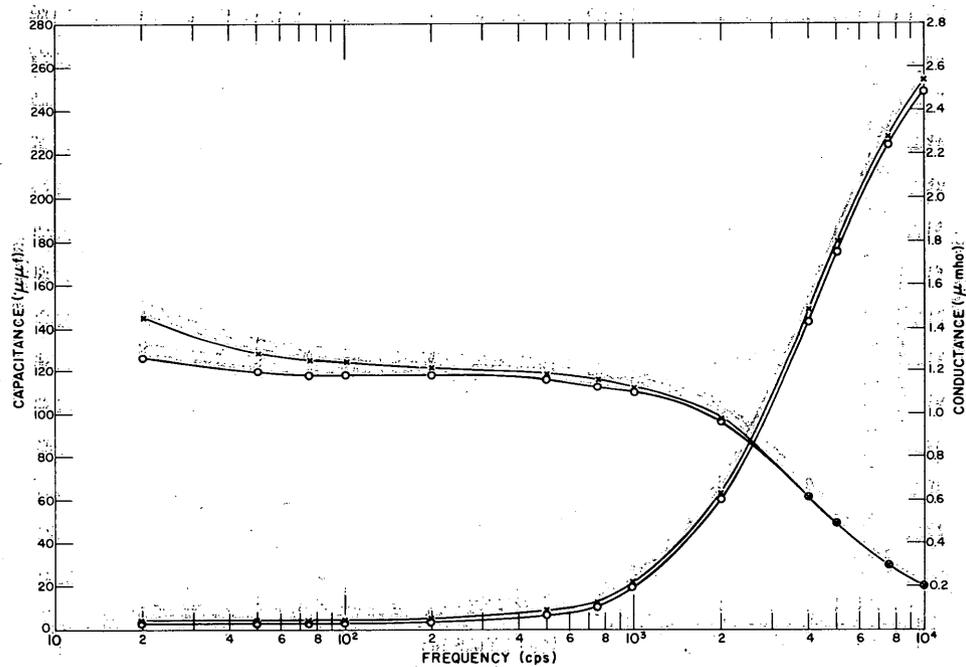


Figure 11. Sample 12 (same as sample 11, but with Lucite jacket removed, brass electrodes).

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

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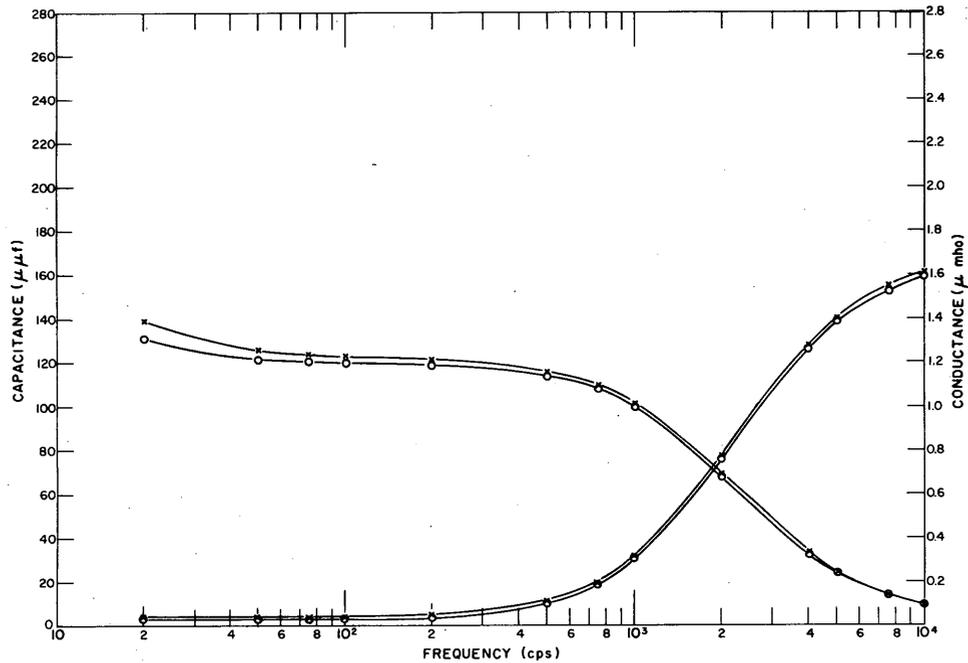


Figure 12. Sample 12, -12C.

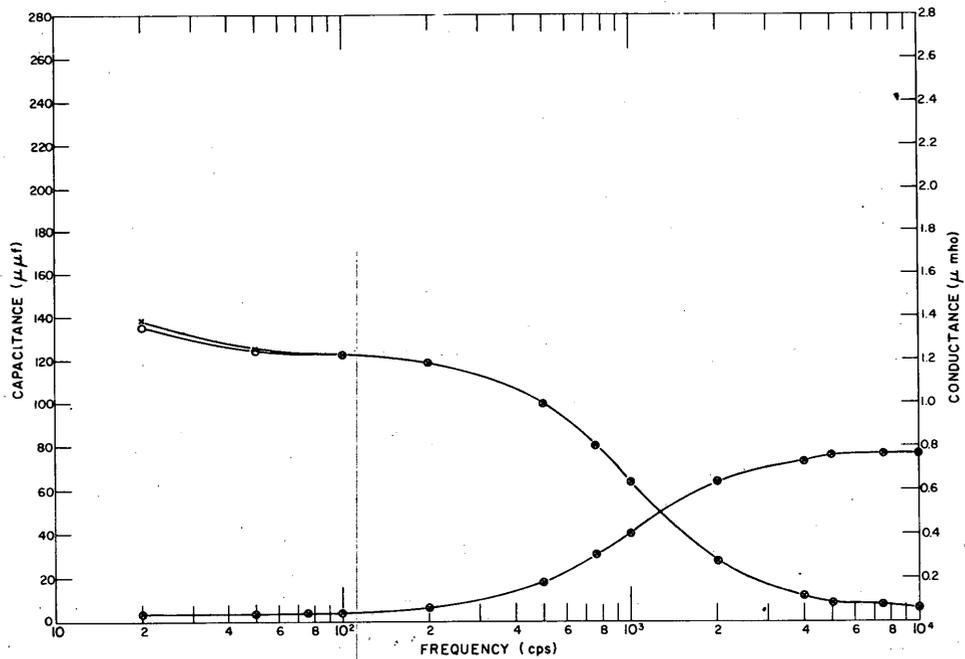


Figure 13. Sample 12, -20C.

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

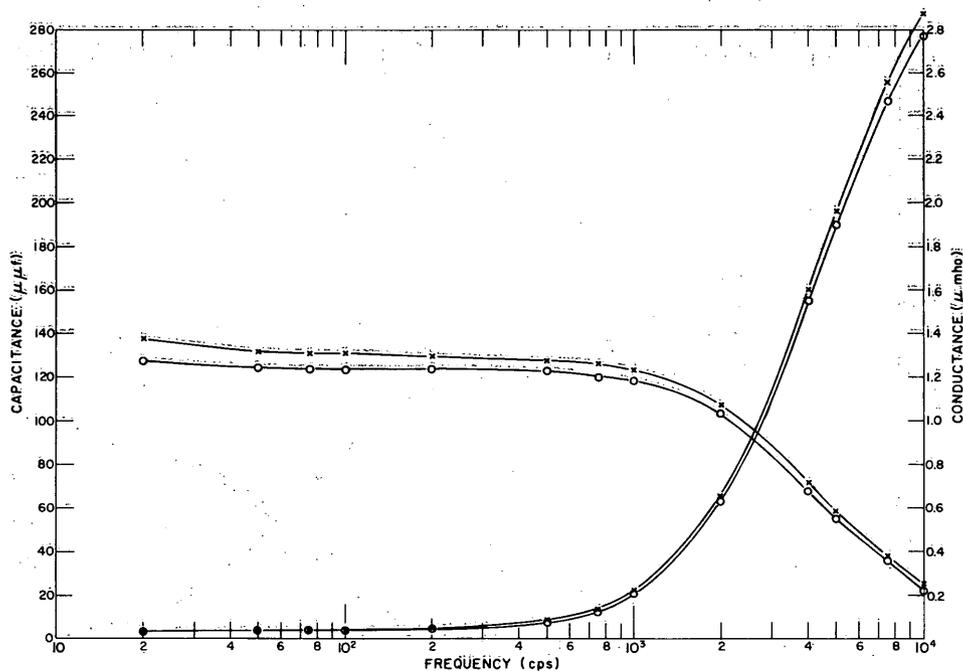


Figure 14. Sample 13, -6.4°C (single crystal sample, cut adjacent to sample 12, platinum plated brass electrodes).

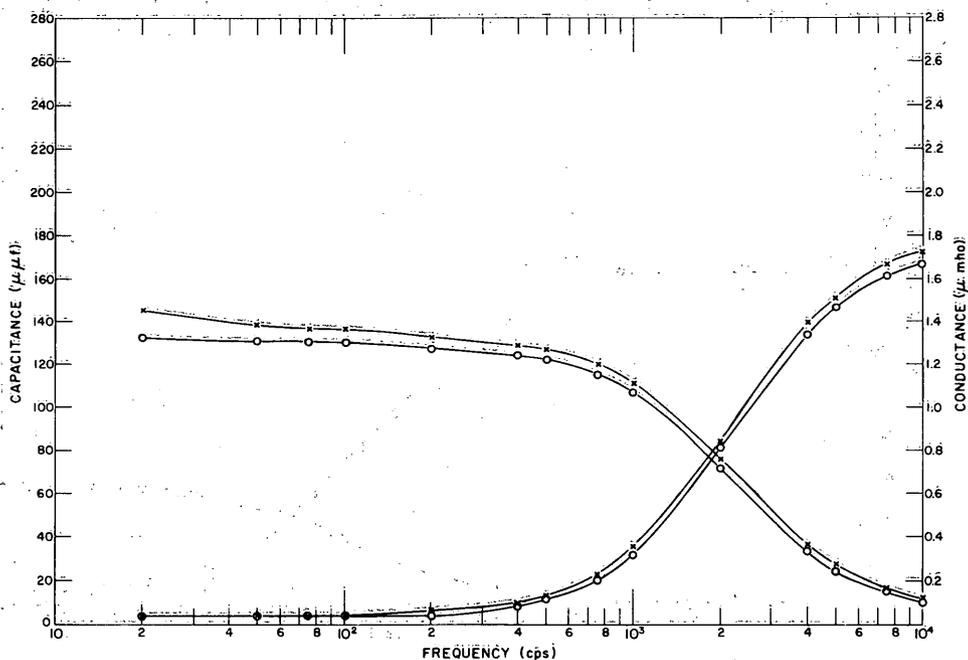


Figure 15. Sample 13, -12.6°C .

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

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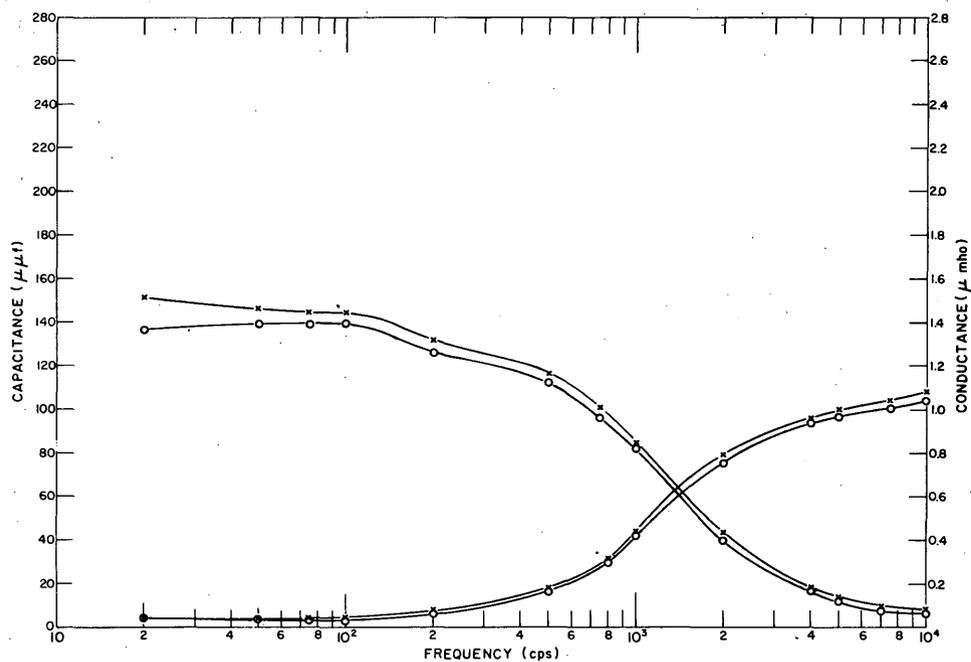


Figure 16. Sample 13, -18.2°C.

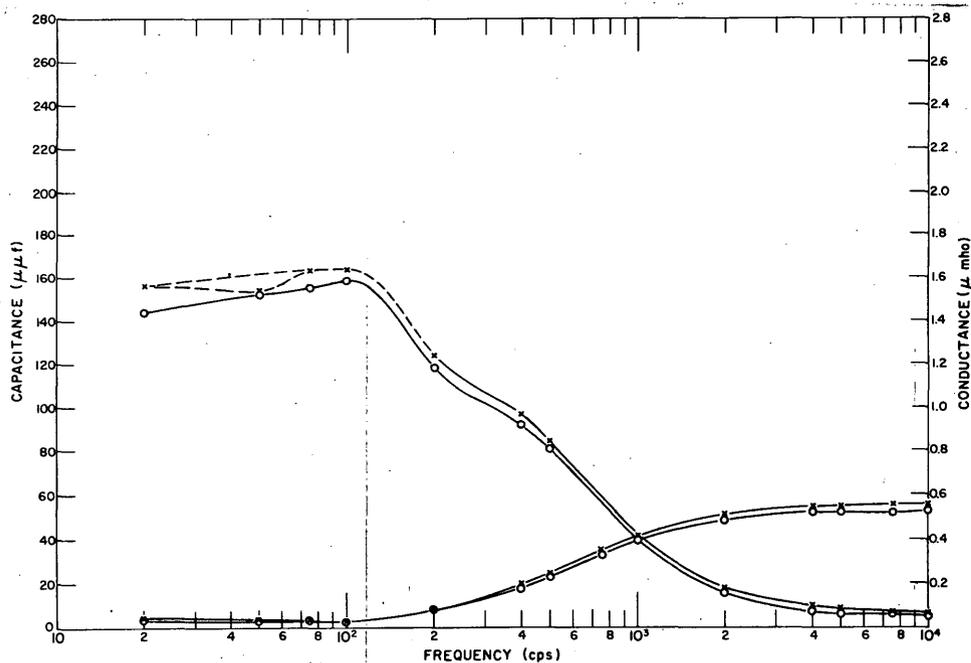


Figure 17. Sample 13, -24.8°C.

Equivalent parallel conductance and capacitance measurements for three-electrode assembly shown in Figure 4. Crosses indicate values for bulk plus surface (ring electrode) and circles indicate values for bulk (center electrode). 2×10^6 ohm-cm water.

It is evident from Figures 5-17 that the dispersion is temperature dependent. If the dispersion is of the pure Debye type, it can be described by the equation (Smythé, 1955, Ch. II)

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} = \epsilon' - j\epsilon'' \quad (9)$$

in which ϵ^* is the complex dielectric constant, ϵ_∞ is the high-frequency dielectric constant (radio frequency, not optical frequency), ϵ_s is the static, or zero frequency, dielectric constant, ω is the angular frequency in radians per second, τ is the relaxation time (sec) characteristic of the material, ϵ' is the real part of the dielectric constant and ϵ'' is the imaginary part of the dielectric constant.

Ordinarily, ϵ_∞ is independent of temperature, $(\epsilon_s - \epsilon_\infty)$ has a slight temperature dependence, varying as $1/T$, and τ has a temperature dependence which obeys an equation of the form

$$1/\tau \equiv \omega_m \equiv 2\pi f_m = A \exp(-E/RT) \text{ radians/sec} \quad (10)$$

in which ω_m is the angular frequency of relaxation, f_m is the frequency of relaxation, E is the activation energy for the relaxation process in kcal/mole, R is the gas constant (kcal/mole deg K) and K is the Kelvin temperature.

We might equally well describe the dispersion in terms of a complex conductivity σ^*

$$\sigma^* - \sigma_0 = \sigma' + j\sigma'' = j\omega\epsilon_0\epsilon^* \quad (11)$$

Here we have added a parallel dc conductance σ_0 to the picture and have designated the real and imaginary parts of the ac conductivity as σ' and σ'' respectively. The real and imaginary parts are

$$\epsilon' - \epsilon_\infty = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} = \frac{\sigma''}{\omega\epsilon_0} \quad (12)$$

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \omega\tau = \frac{\sigma'}{\omega\epsilon_0} \quad (13)$$

where ϵ_0 is the permittivity of free space.

It is evident that

$$\epsilon' - \epsilon_\infty = (\epsilon_s - \epsilon_\infty)/2 \quad \text{when } \omega = 1/\tau. \quad (14)\dagger$$

†Note that $\epsilon_s - \epsilon_\infty$ in our notation is what Jaccard calls ϵ_s .

Determining τ in this way, we have evaluated the constants A and E for samples 11, 12 and 13 (Table I, Fig. 18).

Table I. Frequency factor and activation energy.

Sample	$A/2\pi(\text{sec})^{-1}$	$E(\text{kcal/mole})$
11	2.7×10^{14}	13.3
12	2.9×10^{14}	13.3
13	2.9×10^{14}	13.6

These values are in good agreement with the published literature (Auty and Cole, 1952; Feuersanger, 1947).

A somewhat better but more tedious technique of analysis is to plot $(\sigma - \sigma_0)/\omega$ against $\epsilon' - \epsilon_\infty$ as a function of frequency. The result for a pure Debye dispersion is a semicircle. The frequency for which $\epsilon = (\epsilon_s + \epsilon_\infty)/2$ is the relaxation frequency, $f_m = 2\pi\omega\tau$. This technique, often called a Cole plot (Cole and Cole, 1941), has the advantage that all the points contribute to the determination of the origin and radius of the semicircle. Thus it is more accurate. It is of particular usefulness when the dispersion is not quite a pure Debye type (e.g., for a distribution of relaxation times). The data for sample 11 have been reevaluated in this way and lead to the same results. A Cole plot for sample 13 at -30°C is shown in Figure 19. (Conductance and capacitance are plotted here rather than conductivity and dielectric constant.)

The most interesting feature of these experiments is the difference between the conductance and capacitance values for the ring (bulk plus surface) and those for the disk (bulk). On the basis of our thin rod experiments (p. 9) we would have expected a surface dc conductance of about $6 \times 10^{-7} \text{ ohm}^{-1}$ at -10°C for the ring samples. An added frequency dependent term might or might not appear. However,

for all of these experiments the difference was small and in the low frequency region was even less than the projected dc value. This suggests a large impurity contribution to the dc surface conductance in the slim rod experiments.

The difference in capacitance $[C(\text{bulk plus surface}) - C(\text{bulk}) = \Delta C]$ and in conductance $[G(\text{bulk plus surface}) - G(\text{bulk}) = \Delta G]$ are plotted for a representative polycrystalline sample (9) in Figures 20 and 21 and for the single crystal sample 13 in Figures 22 and 23. Remembering the fact that these are difference curves, they are reasonably smooth and well behaved. It is apparent at once that the shapes of these curves are very similar to those of the parent curves from which they were derived. This would lead us to suppose that they are a consequence of unequal areas of ice

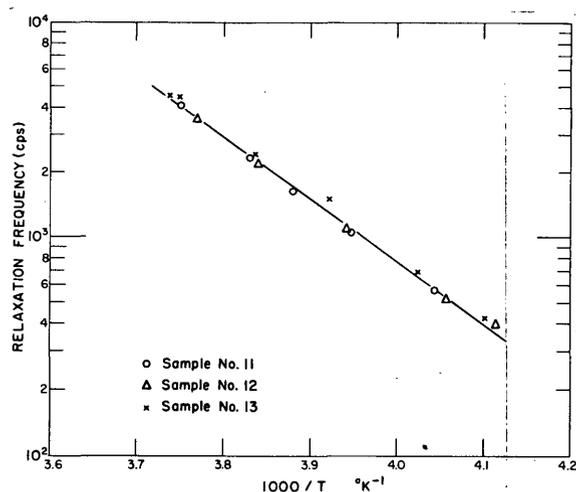


Figure 18. Semi-log plot of relaxation frequency vs $1000/T^\circ\text{K}^{-1}$ for samples 11, 12 and 13 yielding the data of Table I.

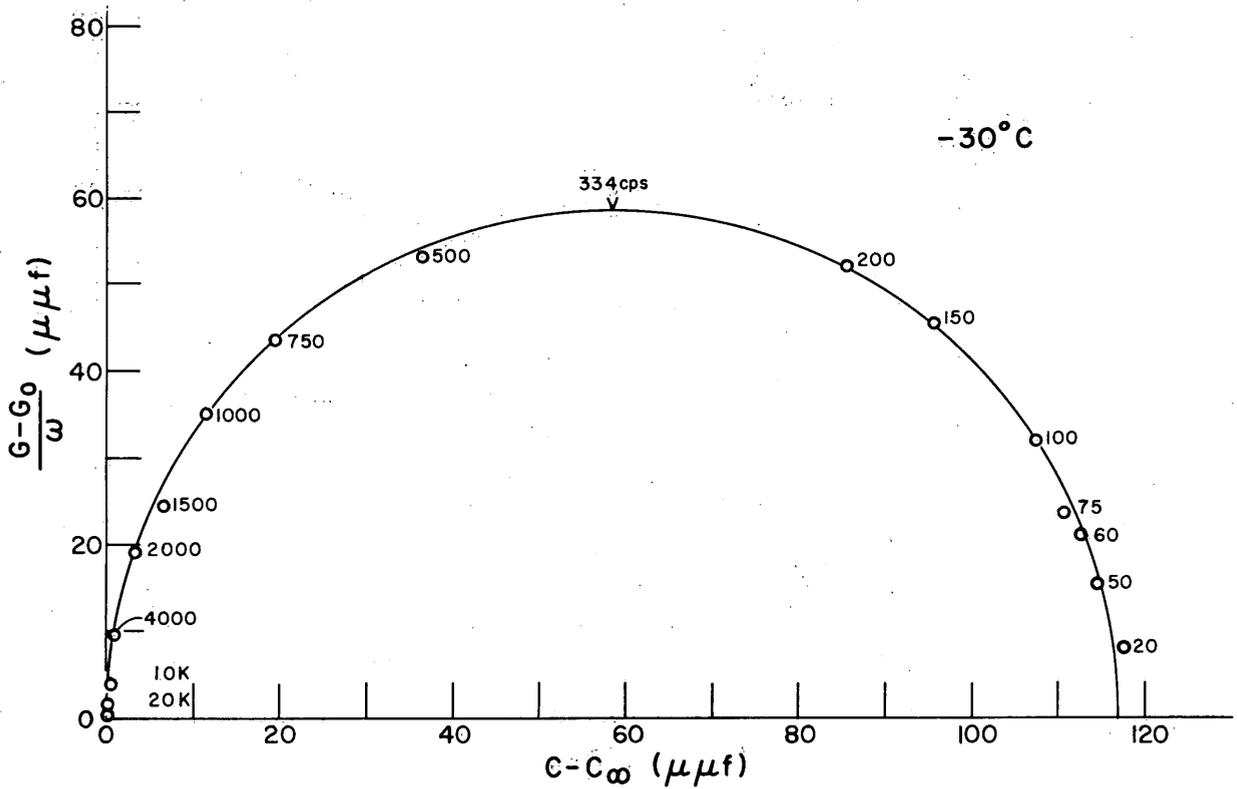


Figure 19. Typical Cole plot (sample 13, -30C).

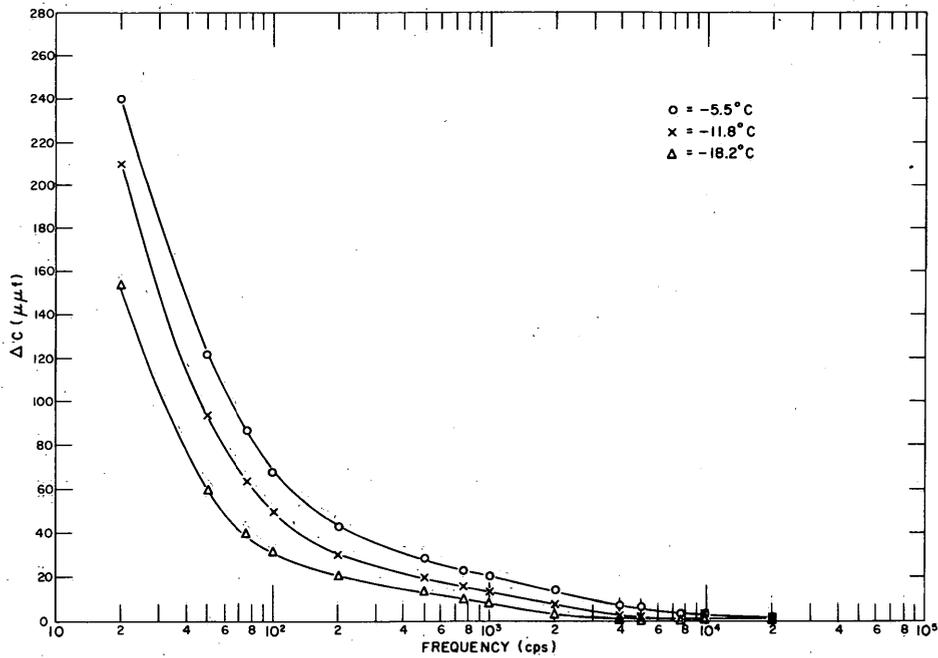


Figure 20. Difference in capacitance (bulk plus surface, minus bulk) vs frequency for sample 9 at indicated temperatures. (Polycrystalline sample from 2 megohm-cm water, brass electrodes.)

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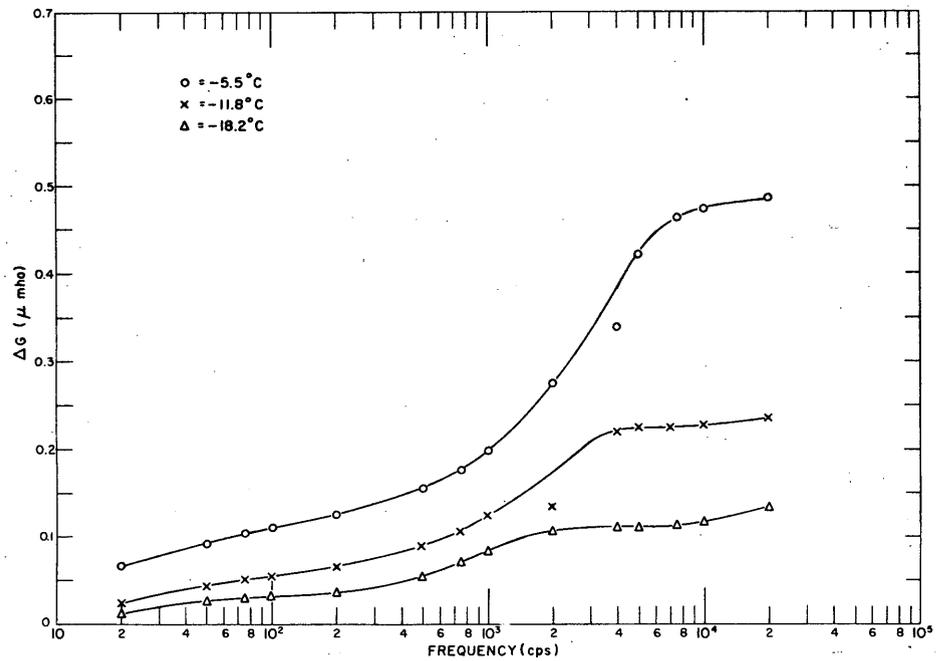


Figure 21. Difference in conductance (bulk plus surface, minus bulk) for sample 9 at indicated temperatures.

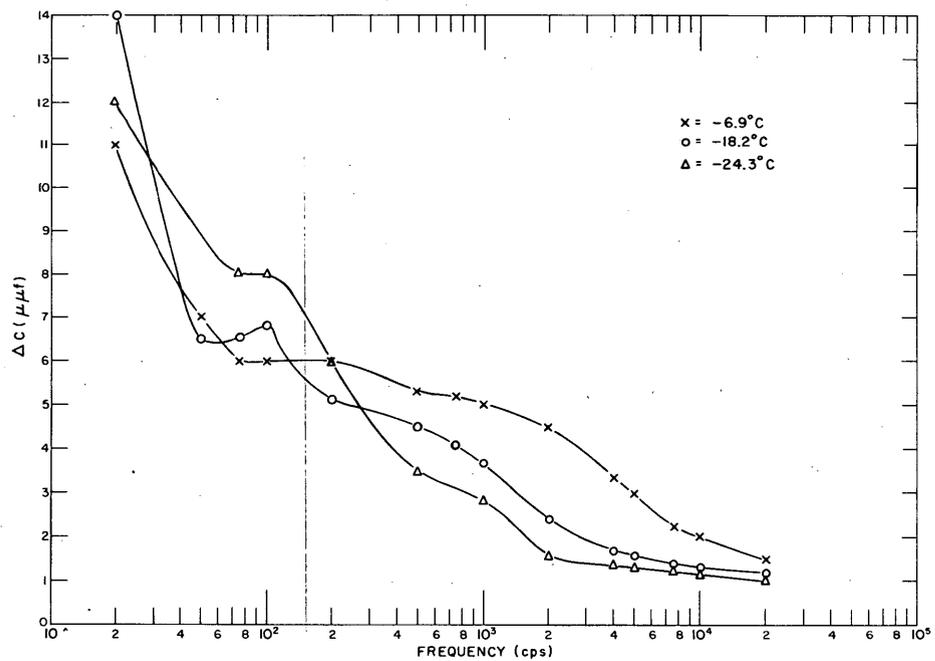


Figure 22. Difference in conductance (bulk plus surface, minus bulk) for sample 13 at indicated temperature (single crystal, platinum plated brass electrodes).

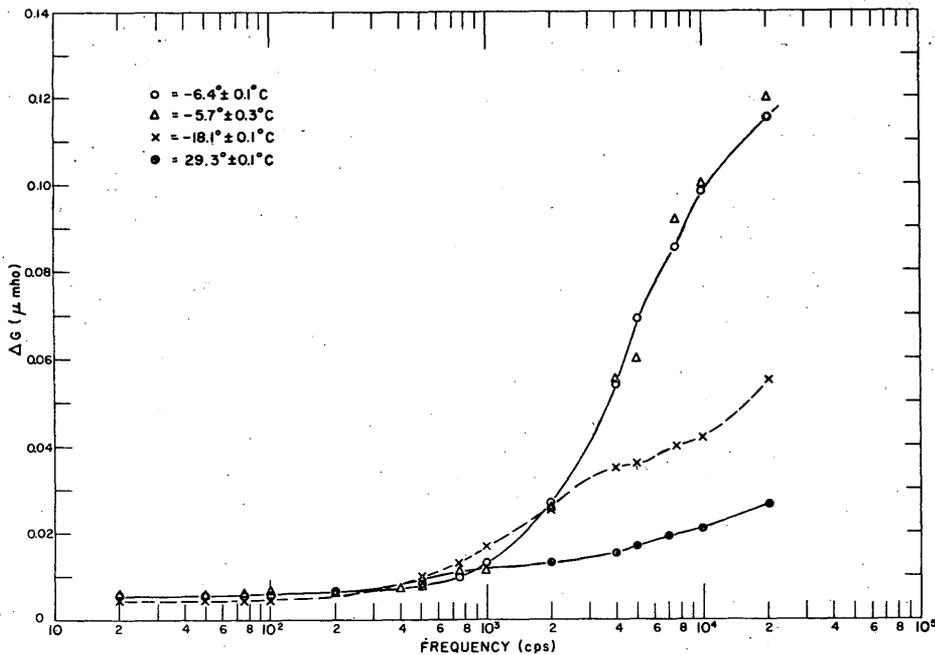


Figure 23. Difference in conductance (bulk plus surface, minus bulk) for sample 13 at indicated temperatures.

under the ring and disk electrodes. We estimate that misalignment of our plates relative to the sample and the possible misfit of the sample due to ellipticity of the Lucite tube in which the sample was grown can account for a difference of a few per cent. The differences here seem to be larger than we can account for in this way. Moreover, a careful look at the differences shows that the frequency dependence is really not in accord with this explanation. For example, it is possible to account for most of the difference ΔC above 500 cycles for sample 13 in this way but not for that below 500 cycles. The trend for the ΔG is also right but the frequency dependence is not what it should be. The situation with sample 9 is much worse. The magnitudes are much too large to ascribe to unequal areas. We accept misalignment as a partial contribution only.

Our experience with growing single crystals has led us to the realization that when impurities are present in a melt they usually do not distribute themselves uniformly throughout the crystal (Camp, 1963, p. 3). This is largely the result of different flow velocities, convection or forced, at different regions of the growing interface. As impurities are rejected to the melt by the growing crystal, they increase the concentration in the melt at the liquid-solid interface. Circulation sweeps them away and tends to reduce the concentration at the interface to the average value in the melt. The presence of an obstacle such as the wall of a tube reduces the circulation, allows greater concentration to build up, and therefore results in a higher concentration in the solid. Thus we believe that although the concentrations are very small indeed, the impurity content of the outer zone (ring) is greater than that of the center region (disk) and that this difference in concentration also contributes to ΔC and ΔG . Such an hypothesis is consistent with the fact that ΔC and ΔG are much larger for sample 9 than for sample 13. On the basis of the way in which they were prepared, and on the low frequency values of bulk conductance, we believe that sample 9 is less pure than sample 13.

We conclude from these experiments that: (1) If an ac effect occurs due to the surface, it is very small, probably no more than 2% of the total for the geometry and size used. (2) The effect of having a sample jacketed with Lucite is negligible (which is itself consistent with 1); (3) Alternating current grain boundary effects in pure crystals are small. (4) Polarization can be reduced both by using platinum electrodes and pure samples (a conclusion which is greatly strengthened by the experiments of Section IV and V). (5) An apparent surface effect can be caused by growing a sample in such a way that there is a higher concentration of impurities near the surface than in the interior.

A frequency-independent surface conductance should simply add in parallel to the frequency-dependent bulk conductance. Thus the low values of ac conductance at low frequencies would imply either a much smaller surface current than found for the slim rod samples or a surface conductance which decreases with rising frequency. Although we had in mind no mechanism which could give rise to a surface conductance larger at dc than at low audio frequencies, dc measurements were made on some of the guard ring samples for the sake of completeness. Because the current was found to vary with time after the voltage was switched on, it was monitored with a recorder. Figure 24 shows the conductivity of both inner and outer zones (bulk and bulk plus surface) of sample 13 measured in this way as a function of $1000/T^{\circ}\text{K}^{-1}$. Two sets of data are given: the first was measured 5 sec and the second 5 min after the voltage was applied. Between measurements, the sample was short circuited for about 30 min.

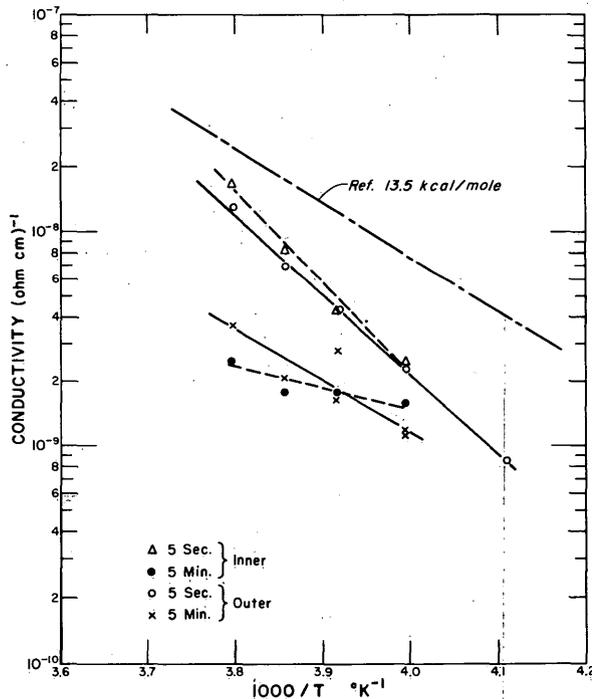


Figure 24. Apparent dc conductivity of sample 13 (single crystal, platinum plated guard ring electrodes) as a function of temperature. Measurements were made of the current through each electrode 5 sec and 5 min after the voltage was applied giving rise to the four sets of data shown.

It is clear from Figure 24 that, when polarization is present, one may obtain very different values of apparent activation energy in a two-probe experiment depending on how much time elapses in each measurement between the application of the voltage and the measurement of the current. Note that although the slopes are about equal for the inner and outer zones for the 5-sec data, the slope at 5 min is significantly greater for the outer zone than for the inner. This suggests that the outer zone is able to depolarize somewhat faster than the inner, which lacks a free surface at the bottom electrode.

Time-dependent currents are an indication of polarization and therefore the conductance values are in doubt in about the same proportions as the current varies with time. Figure 25 shows the current time behavior for sample 12 (single crystal, brass electrodes, no plastic ring) for -10°C and -23°C . It is typical of the data we obtained. At the higher temperatures, the outer (ring) electrode current is only slightly time dependent, while the inner electrode shows a large initial drop and then a fairly stable behavior. At lower temperatures both electrodes show the initial sharp drop followed by a slow

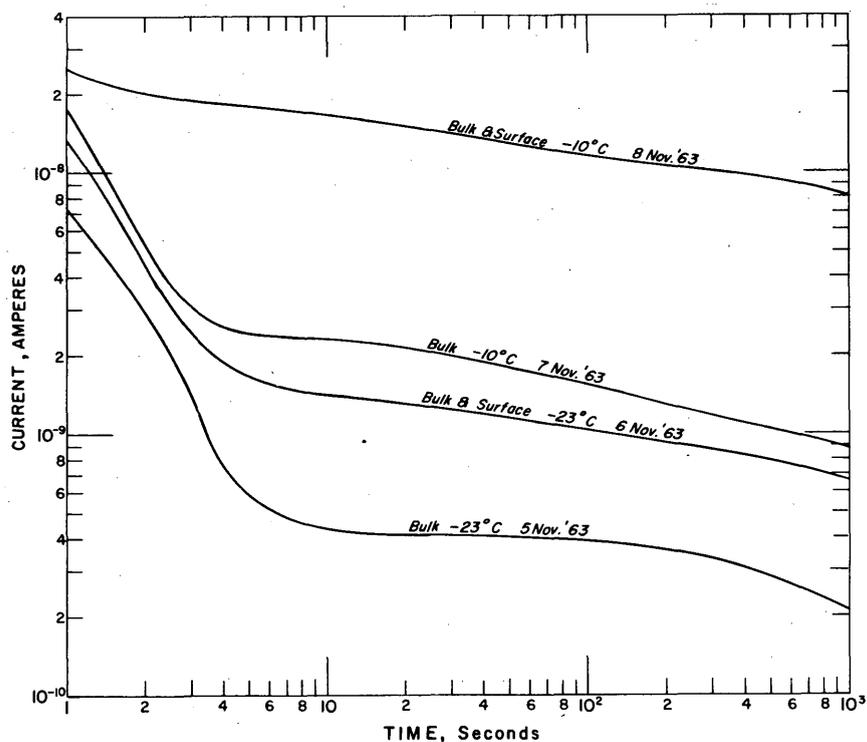


Figure 25. Log-log plot of current versus time for sample 12 (single crystal, brass electrodes) after a constant potential of 10 volts was applied. Both ring and center electrode currents were monitored. Polarization is clearly less for the ring electrode than for the center electrode.

decay. This behavior would be consistent with a model in which there was a nonpolarizable surface current having a large temperature dependence shunting the bulk conductance which was subject to polarization and had a smaller temperature dependence. It is also consistent with a model in which the outer ring shows much less polarization than the inner. This could be the case if depolarization takes place at the edge of the electrode where air, ice and metal meet. Both zones have free edges of this kind at the top electrode, but the bottom electrode is solid and only the outer zone has a free edge.

Slim rod experiments

In order to clarify the questions raised by the foregoing experiments, it seemed necessary to repeat the slim rod experiments using better technique and water of very high purity. (As is discussed in the next section the latter eventually became available.) A polycrystalline rod sample was prepared from 15 megohm cm water in a well leached Teflon tube of 1/8 in. inside diameter. The tube contained six platinum wire electrodes. The two end wires served as current electrodes and measurements between adjacent pairs showed a uniform potential distribution along the sample and a small polarization at the current electrodes. The high temperature part of these data is shown in Figure 26 (A). Above -30°C , the conductivity is almost constant. The wires were then removed permitting the sample to be extracted. A section of rod adjacent to the one on which these measurements were made was extruded onto a framework of four platinum wires in a large polyethylene tube. Two of these served as current electrodes and two as voltage probes. Measurements taken in this configuration are shown in Figure 26 (B). The conductance

ELECTRICAL CONDUCTION IN ICE

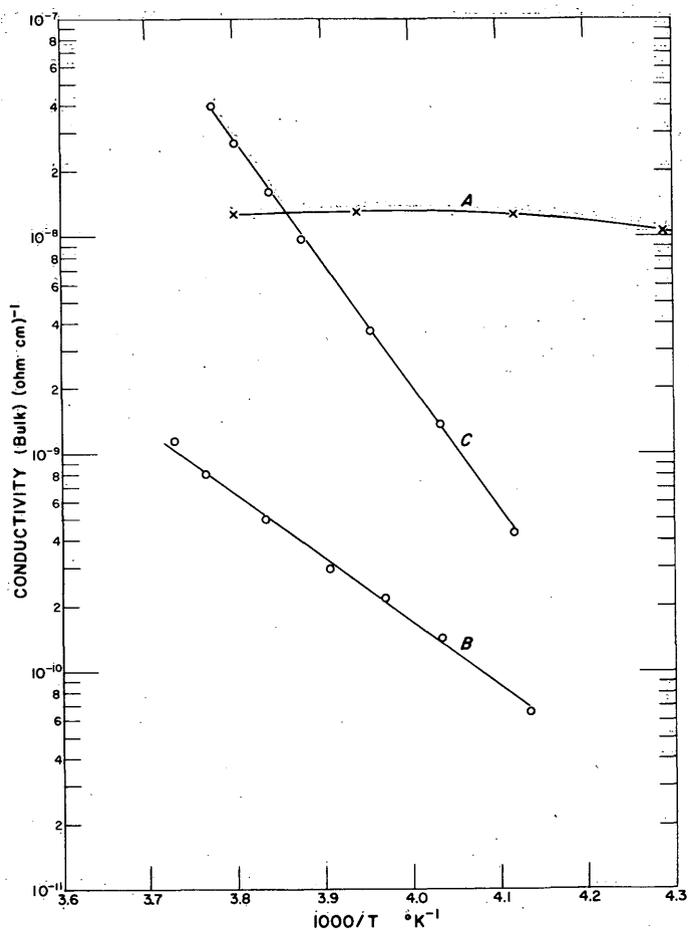


Figure 26. Direct current conductivity vs $1000/T^{\circ}\text{K}$ for slim rod experiments using high purity water (four-probe). A. 1/8 in. rod encased in Teflon; B. Sample adjacent to A after extrusion from the Teflon tube; C. Sample B after deliberate contamination of the surface.

is one to two orders of magnitude smaller than in A and has a strong temperature dependence. Finally, the surface of the bar was deliberately contaminated by running a finger along its length. It was then remeasured with the results shown in Figure 26(C). (The conductivity is calculated as a bulk conductivity.) The difference between branches A and B is surprising but it must be remembered that different samples were measured. More important, inspection of both samples showed that B contained bubbles while A was clear. The difference between B and C was clearly caused by surface treatment.

We thus seem to be led to the view that a clean surface contributes very little to the total conductance of a sample of the sizes considered here but that it is very easy for a large surface current to arise due to surface contamination. When we consider the actual numbers involved, we find that for the contaminated case the concept of simple surface conductivity is not adequate. It is shown in Appendix A that high activation energies for conduction necessarily imply low values for conductivity when $E \gg RT$ ($R =$ gas constant, $T =$ temp, Kelvin). That is, the pre-exponential term in the Arrhenius equation cannot be arbitrarily large. For

conduction in the surface layer, it is shown that an activation energy of 19 kcal/mole implies a surface conductivity of less than 3.2×10^{-20} ohms $^{-1}$ at -10C. This is in serious conflict with our measurements which appear to give values in excess of 10^{-8} ohms $^{-1}$. This difficulty stems at least in part from regarding surface conductance as occurring only in the surface monolayer.

More properly, we should define surface conductance as that portion of the conductance which occurs because of the presence of a surface. If the surface imposes a disorder in the lattice which extends many layers below the surface layer, the conductivity of this whole disordered region may be altered. It is this change which we must regard as the surface contribution. Clearly this definition allows negative as well as positive values for surface conductivity.

However, even this concept of surface conductivity does not reconcile our data for the slim rods. In the extreme case of a very thick layer, we would calculate bulk conductivity. Our slim rod values are then in excess of 10^{-7} (ohm cm) $^{-1}$ and Appendix A shows that the maximum bulk conductivity we can account for in this way, having an activation energy of 19 kcal/mole, is 10^{-12} (ohm cm) $^{-1}$. We are forced to conclude that the temperature dependence we have measured does not give the activation energy for conduction.

A way out of this dilemma can be found if we modify our model. If the effective thickness of the disordered layer is itself a strong function of temperature, we can have a specific conductance in this region which has a low activation energy (and hence can have a large value). The temperature dependence of the measured conductance will still be large because the thickness of the current-carrying layer is strongly temperature dependent. It is immaterial whether the heightened conductance is caused by the disorder itself or the presence of impurities in the disordered layer. It does seem quite reasonable that a disordered structure should be a better host to impurities such as dissolved gases than a perfect lattice. (The idea of a disordered surface region many atom layers thick having properties quite different from those of ordinary ice is one which has received much support in recent years based on a variety of different experiments. Jellinek* has reviewed this subject.)

As an example, consider a cylindrical sample of radius r and of unit length. Let a very thin region of thickness $\delta \ll r$ at the surface be disordered. (This is unreal in the sense that we expect the disorder to be a smooth function of the distance from the surface. However we can describe this region by an effective thickness δ which is chosen to give the same conductance as the true disordered region.) Let the conductivity of the inner core be σ_1 , and that of the disordered region be σ_2 . Let the thickness δ vary as

$$\delta = \delta_0 e^{-\theta/T} \quad (15)$$

where θ is a constant having the units of temperature. The total conductance G of the sample will be (for the approximation $\delta \ll r$)

$$G = \frac{\pi r^2}{l} \sigma_1 + \frac{2\pi r}{l} \delta \sigma_2 \quad (16)$$

*Jellinek, H.H.G. (1961) Liquidlike layers on ice, Journal of Applied Physics, vol. 32, no. 9, p. 1793.

where l is the sample length, and the apparent conductivity σ_a will be

$$\sigma_a = \sigma_1 + \frac{2\delta}{r} \sigma_2 \quad (17)$$

For sufficiently large samples σ_1 will dominate. However in the case which interests us here $\sigma_a \gg \sigma_1$, and therefore

$$\sigma_a = \frac{2\sigma_2 \delta_0}{r} e^{-\theta/T} \quad (18)$$

If $\sigma_2 = A_2 e^{-E_2/RT}$ (that is, if it obeys the Arrhenius relation) we have

$$\sigma_a = \frac{2A_2 \delta_0}{r} e^{-(\theta R + E_2)/RT} = A e^{-E\sigma_a/RT} \quad (\text{where } A \equiv \frac{2A_2 \delta_0}{r} \text{ and}$$

$E\sigma_a \equiv R\theta + E_2$) which also is of the Arrhenius form. But $E\sigma_a$ is no longer the energy of a molecular process.

As a specific example, suppose $\delta = 10^4$ and $R\theta = 13.5$ kcal/mole. These numbers are so chosen that δ falls in the range predicted by various authors* and has an activation energy approximately equal to that required to break two bonds per molecule. At -10°C , $\delta = 7 \times 10^{-8}$ cm. From our experiment $E\sigma_a = 19$ kcal/mole $= R\theta + E_2$. Therefore $E_2 = 19 - 13.5 = 5.5$ kcal/mole is the activation energy for σ_2 .

From eq A13 (App. A) the maximum value σ_2 can have at -10°C is 1.6×10^{-1} (ohm cm) $^{-1}$ for this value of E_2 . Thus the apparent conductivity, σ_a , must be less than 1.4×10^{-7} (ohm cm) $^{-1}$.

Clearly this is of the right order of magnitude to explain our results. Had we divided $E\sigma_a$ differently between $R\theta$ and E_2 or chosen a different value for δ at -10°C we could have obtained almost any number we wished. Thus while the numerical example we chose has a special interest, we can only say that this kind of explanation can easily account for the values we have measured.

IV. IMPROVEMENTS IN TECHNIQUE

From the surface experiments of Section III it was clear that for uncontaminated surfaces, surface conduction did not play a dominant role when techniques of only moderate purity were employed and large diameter samples were used. Thus we must consider several other possibilities for explaining the variety of results found by previous investigators. They might have been caused by contaminated surfaces. They might somehow be the result of bulk impurities. Or our own samples might have contained bulk impurities in sufficient quantity so that the bulk impurity conductance masked the surface conductance. This might then become important at higher purity. Therefore a serious attempt was made to prepare samples of the highest purity. Because, if possible, we wished to use a guarded ring technique for our measurements, a systematic attempt was also made to reduce polarization and the consequent need for four-probe measurements.

*See for example, N.H. Fletcher (1962) Surface structure of water and ice, Philosophical Magazine, vol. 7, p. 255-69 and a subsequent correction, Phil. Mag., vol. 8, (1963), p. 33. See also J.W. Telford and J.S. Turner (1963) The motion of a wire through ice, Phil. Mag., vol. 8, p. 527-531. The idea of the disordered surface region goes back to Faraday.

Water purity

In the previous single crystal experiments, the samples had been prepared from water which was first distilled, giving a conductivity at 25°C of about $1.6 \times 10^{-6} \text{ (ohm cm)}^{-1}$. It was then passed through a Crystalab demineralizer (Model CL-5) which reduced the conductivity to about $5 \times 10^{-7} \text{ (ohm cm)}^{-1}$. Samples were prepared by filling a Lucite tube with this water, chilling it to 0°C and inserting a seed crystal at the bottom. The system was evacuated for 30 min to remove dissolved gases and then the sample was slowly frozen from the bottom up (see Fig. 27a). In order to mount the samples, they had to be cut and frozen onto the electrodes, processes which also introduced contamination.

A search for means of obtaining purer water revealed that block tin lined stills are reported capable of producing water having a conductivity roughly an order of magnitude lower than that obtainable from commercial Pyrex or quartz stills (Smith, n. d.). The Barnstead Models E-1 and E-2 are said to produce water of $7 \times 10^{-8} \text{ (ohm cm)}^{-1}$ at a rate of 2 liters per hour. Barnstead also markets a mixed bed ion exchange resin (Model HN8902) which purifies water so that its conductivity is about $5.5 \times 10^{-8} \text{ (ohm cm)}^{-1}$ at room temperature. Although an ion exchange column does not remove organic materials or particles, this type of purification is not only much cheaper than distillation but is much more convenient. The water is at room temperature, it is available when it is needed, and the apparatus takes up little space. Since particles and organics should have little effect on the conductivity and should be strongly rejected by the ice anyway, this system was chosen.

In order to minimize the organic and particulate material and to lengthen the life of the mixed bed demineralizer, we connected the HN8902 column in series with the older system. Thus laboratory quality distilled water was passed through a Crystalab Model CL-5 demineralizer and thence through the mixed bed column. Since Teflon is reported (Smith, n. d.) to be among the best plastic materials for the storage of high purity water, Teflon tubing and sample cells were used.

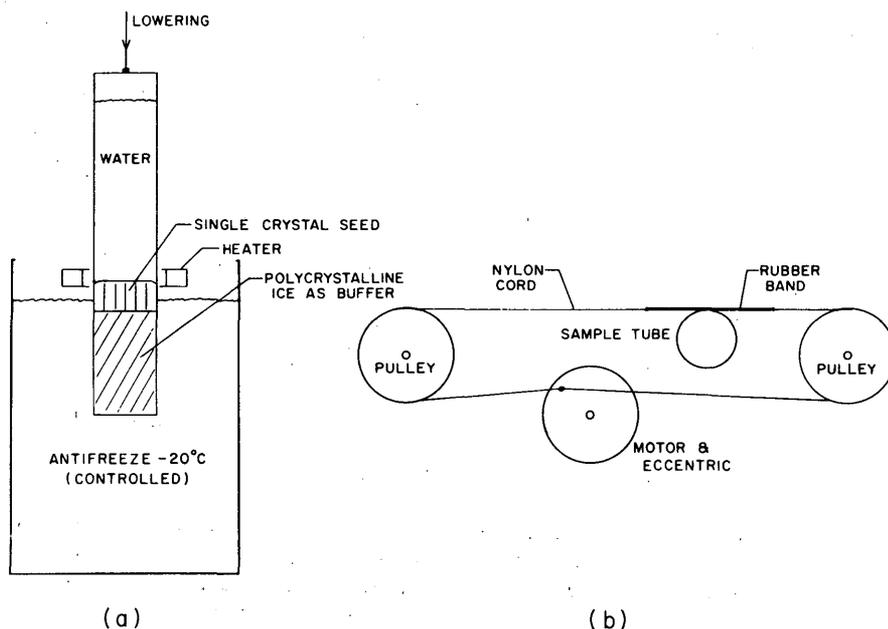


Figure 27. a. Apparatus for growing single crystals of ice from air-free water. b. Agitation mechanism to prevent bubbles and concentration of impurities near the wall in small tubes.

Polarization

In the guard ring experiments of Section III, electrical contact to the sample was made by melting the electrodes onto the surface of the ice crystal. When dc measurements were made using a constant applied voltage, the current was found to decrease sharply for the first few seconds after application of the voltage and then to continue to drop but much more slowly. This behavior was more pronounced for the disk current than for that of the outer ring (see Fig. 25) which suggests that the presence of a free surface at an electrode helps to dissipate whatever is causing the polarization or electrode blocking. By means of a four-probe experiment this blocking can be shown to be localized in the region of the current electrodes. Figure 28 shows a typical four-probe configuration and the voltage measurements made across adjacent pairs of electrodes after a constant potential had been applied for 3 hours. It also shows the voltage-current characteristics when the voltage is measured by means of an electrometer between the two center (voltage) electrodes. It is seen that the ice is ohmic (linear voltage-current plot) and that the principle voltage drop is in the vicinity of the anode. At the time the voltage was first applied, almost half of the drop occurred across the center electrodes.

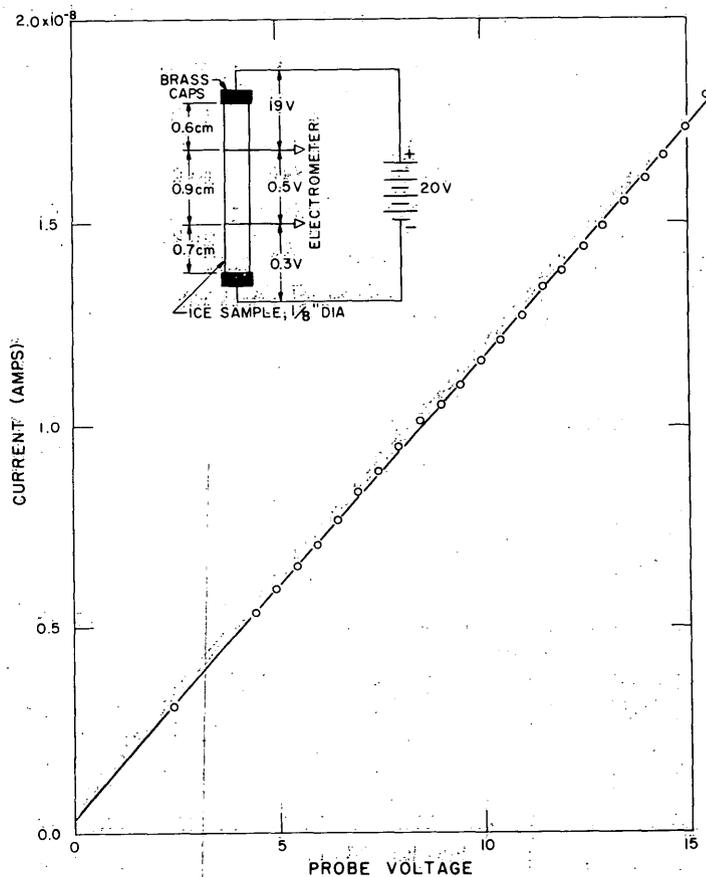


Figure 28. Typical four-probe dc measurement showing the potential distribution after 3 hours of current flow and also showing the linearity between sample current and probe voltage.

A set of 4-probe experiments was performed using current electrodes of various materials: copper, brass, aluminum, nichrome, tin, platinum, platinum black and rhodium. Of these the best were platinum and platinum black with rhodium a fair third. Cleaning the electrodes in nitric acid before using them also improved their behavior. Some difficulty was encountered with platinum black in that it tended to become contaminated and then was hard to clean. Even clean platinum electrodes tended to polarize if they were frozen onto ice samples which had been exposed to air. The best results were obtained when the ice sample was grown in a cell which contained clean platinum electrodes. These electrodes gave nearly ohmic contacts.*

Sample preparation

The samples were prepared in tubes (usually Teflon) which had been scrubbed with Alconox†, then rinsed repeatedly in distilled water, then soaked in demineralized distilled water for many hours and finally rinsed several times with our best water and filled. The tubes were sealed and pumped for half an hour to remove gases which dissolved as the tubes were being filled. They were then lowered slowly into an antifreeze solution at about -25°C. In this way ice grew from one end to the other. A common growth rate was 3 mm/hr although slower or faster rates were sometimes used. When single crystals were to be grown, the water was chilled to 0°C and a seed crystal, mounted on a stem of buffer ice long enough to provide suitable thermal coupling to the bath, was inserted in the bottom of the tube. The tube was then immersed in the antifreeze solution to within about 1 cm of the liquid-solid interface before lowering was started (Fig. 27a). On those occasions when ion exchange resin was put in the sample tube, the system was not usually evacuated. The resin devoured the adsorbed gases.

In the case of small diameter tubes, pumping became impractical. In such instances care was taken in filling to insure that the dissolved gases were a minimum and the tubes were filled to the brim. A tiny pinhole was left at the top through which water could be extruded to compensate for the expansion of freezing. Even with these precautions and slow growth, some gas was dissolved in the water and formed bubbles in the ice.

The formation of bubbles in ice grown in small tubes was believed to be partly the result of inadequate natural convection. Therefore agitation was provided (Fig. 27b). As the sample tube was lowered axially into the cold bath it was rotated back and forth about its axis by means of a belt driven by an eccentric pulley. Thus it was constantly in accelerated rotary motion and the acceleration was greatest at the walls of the tube where turbulence was most desired. This method gave bubble-free samples even for tubes as small as 1/8 in. diam.

The conductivity of the water was measured in the sample tubes after they had been filled, either using the same electrodes which were later used for ice conductivity measurements or using auxiliary electrodes inserted for that purpose. The electrodes were calibrated by measuring the interelectrode capacitance C with water in the tube and using the relationship

$$\rho = \frac{RC}{\epsilon_0 \epsilon_w} \quad \text{or} \quad \sigma = \frac{\epsilon_0 \epsilon_w G}{C} \quad (20)$$

*Gross (in press) reports that sintered platinum and palladium filters carefully cleaned make excellent nonpolarizing electrodes. They are available from Englehard Industries, Inc., Newark, New Jersey.

†A laboratory detergent made by Alconox, Inc., New York 3, New York.

where ρ = resistivity to be found = $1/\sigma$

R = resistance measured = $1/G$

ϵ_w = dielectric constant of water, about 80

ϵ_0 = permittivity of free space; 8.85×10^{-12} farad/meter

It was found that even under the best conditions (except when the ion exchange resin was placed directly in the tube) the conductivity rose gradually after the tube was filled. A typical rate for a 1.3 cm diam Teflon tube was an increase in conductivity of about 10^{-7} (ohm cm) $^{-1}$ in 20 min. In general, the smaller diameter tubes contaminated the water more rapidly than did the larger ones. This is consistent with the walls being the source of contaminant.

As has been mentioned previously, one way of overcoming this contamination is to put some of the ion exchange resin inside the sample tube. If this is done and an air space is allowed for expansion, the conductivity of the water is observed to increase initially and then to decrease again. We believe that this is due to the dissolving of CO_2 and its subsequent entrapment in the resins. Occasional agitation is helpful during this process. In this way, room temperature water conductivity as low as 6×10^{-8} (ohm cm) $^{-1}$ has been maintained for days. However, when ice is grown from the bottom up, the resin is trapped in the first ice to grow. Then some contamination of the water can occur while the rest of the sample is freezing.

To avoid this problem, the resin may be contained in a bag of some inert material suspended near the top of the sample tube, the ice sample may be grown from the top down, or, probably best of all, a circulating system may be arranged so that the growing crystal interface is continually flushed with nearly 0C water fresh from a demineralizer column. Such a system was constructed (Fig. 29). Water passes through the demineralizer system at nearly 0C, through the sample tube and back through a circulating pump to the demineralizer system. Meanwhile, the sample tube is being lowered slowly into a cold bath. With this apparatus, water of very high purity is maintained in the system during the whole period of sample growth and the flow provides good circulation at the freezing interface.

V. HIGH PURITY EXPERIMENTS

It is clear from the experiments discussed previously that high purity water and very clean technique are required if good dc or low temperature ac data are to be obtained. Accordingly, when very low conductivity water became available, a series of experiments was performed to redetermine the bulk ac and dc properties of ice. Two types of apparatus were used, the multiprobe and the guarded ring assemblies. The multiprobe experiments allowed us to determine if there was electrode polarization and if there was any serious inhomogeneity in the sample. They also permitted electrode polarization to be circumvented when it was present. Since multiprobe structures must be calibrated and since the calibration for the kind of structures we used is somewhat frequency dependent, they are best for experiments in which relative measurements are being made. Guarded ring measurements are more precise and largely eliminate the effects of contamination of the outer surface of the sample. They also permit simple and excellent shielding and the elimination of stray capacitances.

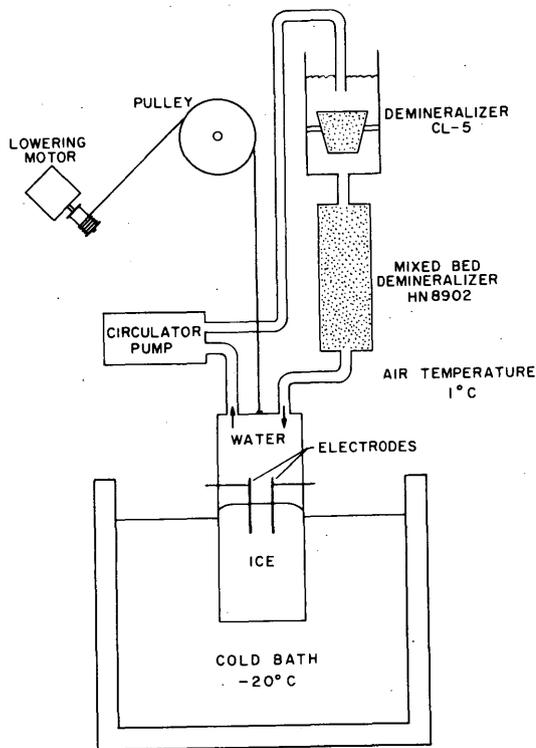


Figure 29. Experimental arrangement by which the growing interface is continually flushed with demineralized water at about 0C.

Multiprobe experiments

The first high purity experiment used a Teflon tube 1.3 cm in diameter into which six platinum wires had been sealed at intervals of 1.3 cm. These wires simply passed diametrically across the section. The tube was thoroughly cleaned with Alconox, leached with 15 megohm-cm water, flushed, filled to overflowing and capped with a fitting which allowed water to squeeze out as ice grew in the tube. The tube was slowly lowered into a freezer so that ice froze up from the bottom. The details of this operation have been described in section IV. The resistivity of the water as measured in the tube after it had been filled was 11 megohm-cm. The ac conductance and capacitance for this sample were measured as functions of frequency at temperatures from -10C to -90C. Some of these data are plotted in Figures 30, 31 and 32. The frequency of the Debye dispersion decreases as temperature falls and eventually (-60C) the dispersion in capacitance is at too low a frequency to be seen. Meanwhile the dispersion in conductance also moves toward lower frequency and decreases in amplitude.

The slight hump in the conductance maximum is believed to be an artifact of measurement possibly caused by the geometry of the electrodes or the fact that the conductance being measured is so small that leakage paths are inadvertently included. The sudden increase in low temperature, low frequency capacitance at -70C is anomalous. We do not find either of these variations in data for the guarded samples where the capacitances and conductances being measured are much larger.

Four-probe dc measurements were also made on this sample over a wide temperature range. The dc conductivity and high frequency ac conductivity measurements for various temperatures are summarized in Figure 33. There are two remarkable features of these data. The first is that the dc conductance is nearly independent of temperature down to -40C. In fact it rises slightly (about as $1/T^\circ\text{K}$). The second is that it begins to fall off rapidly just as the high frequency ac conductance, which has behaved normally at higher temperatures, begins to almost level off. This is behavior which we believe has never been reported but which is reproducible and characteristic of our best technique as will be seen.

In order to confirm the data of Figure 33, a new sample was grown in the same tube. This time the tube was thoroughly flushed by running 18 megohm-cm water through it for several minutes before sealing it off. After the ice had grown to well above the electrodes, the resistivity of the remaining water was measured and found to be greater than 5 megohm-cm. The dc and high frequency ac conductances for this sample are plotted as functions of temperature in Figure 34 (a, b). The behavior is quite similar to that of Figure 33 except that the dc conductance is lower, the $1/T$ region is longer and the break in the ac curve comes at a lower temperature.

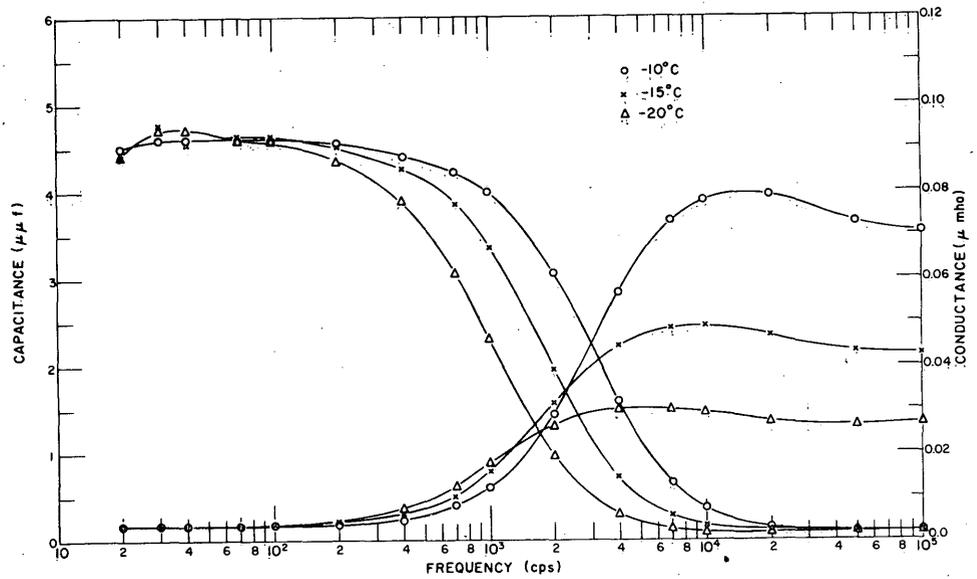


Figure 30. Conductance and capacitance data for indicated temperatures. 1.3 cm diam, rod-type, six-probe polycrystalline sample grown in the Teflon measurement tube.

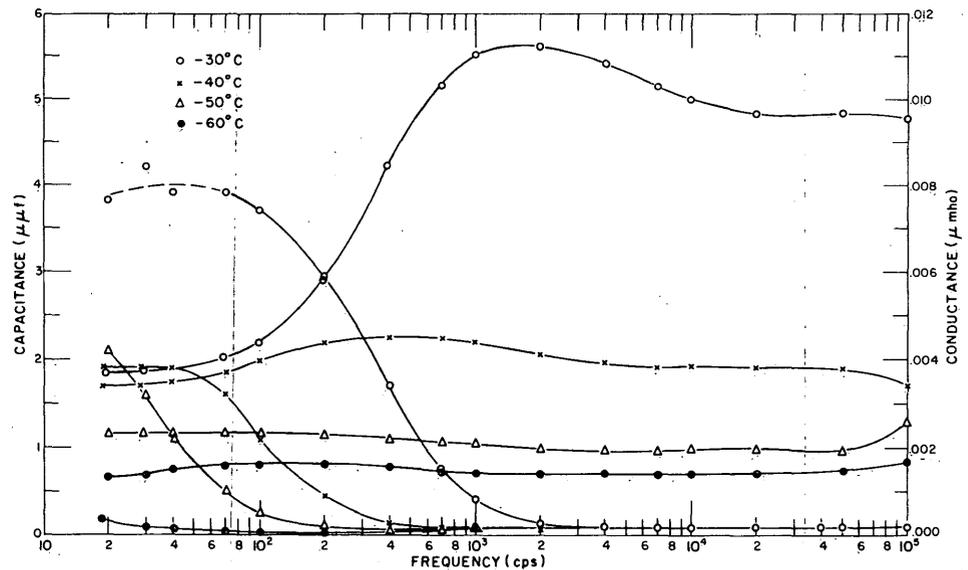


Figure 31. Conductance and capacitance data for sample of Figure 30 at indicated temperatures.

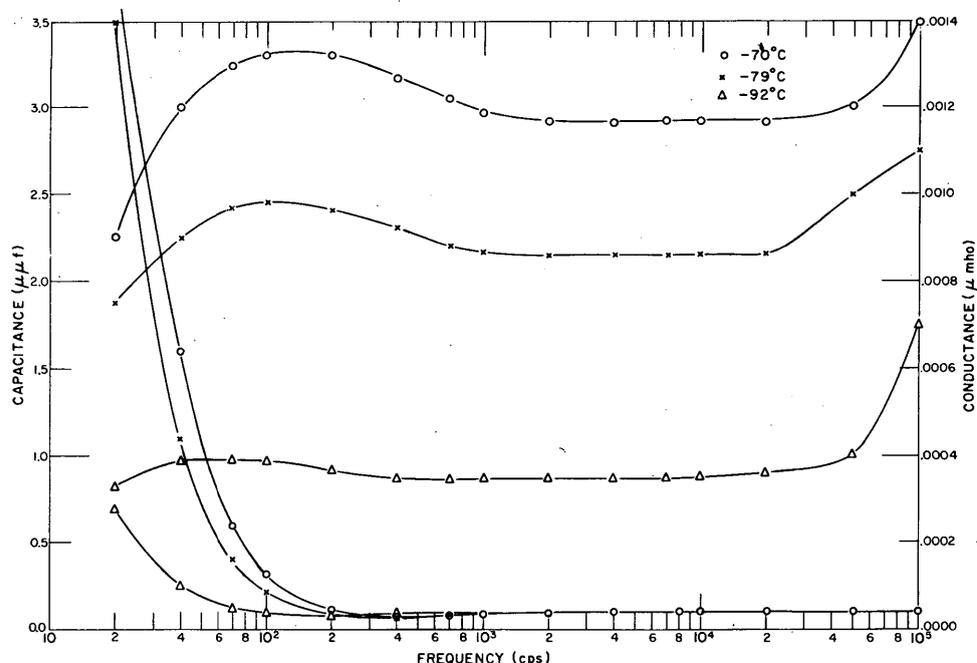


Figure 32. Conductance and capacitance data for sample of Figure 30 at indicated temperatures.

High temperature dc data for a similar multiprobe sample grown in a small diameter (1/8 in.) Teflon tube using clean technique and 15 megohm-cm water have already been mentioned in Section III. These measurements were continued at low temperature with the result shown in Figure 35(a). Because of the high surface to volume ratio of this sample and because, as discussed in Section IV, we have found that this led to contamination from the walls, we believe this sample to be less pure than either that of Figure 33 or 34. The data are consistent with this expectation, the dc conductance being greater than for either Figure 33 or 34.

After these measurements were made on this sample, it was stored for 5 days at -20C. It was then remeasured with the surprising result shown in Figure 35(b). The conductance at -10C had increased by a factor of about 5. Perhaps this indicates continued contamination of the sample by the walls even after it had become solid. The point will be discussed later.

In an attempt to achieve still higher purity, a new six-probe apparatus was constructed in a 1 1/8 in.(3.2 cm) diam Teflon tube. The platinum probes were set 1.3 cm apart. Some of the mixed bed demineralizer resin used in the final stage of purification was placed in the bottom of the tube and it was filled with water which measured 16.4 megohm-cm resistivity immediately after the tube was filled. An air space was left at the top of the tube to accommodate expansion. Forty-five minutes after the system had been sealed, the resistivity, as measured by electrodes in the system, had only fallen to 14 megohm-cm. The sample was then frozen from the bottom up with simultaneous rotary agitation. When half of the water had been frozen, the resistivity of the remaining water was found to be 5.9 megohm-cm at 0C.

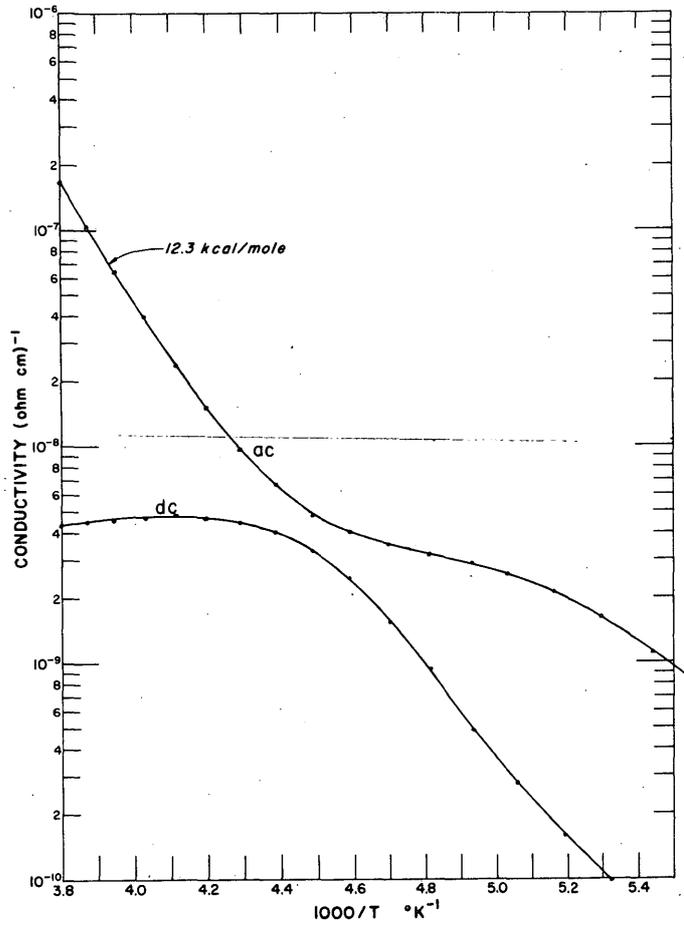


Figure 33. Four-probe dc conductivity measurement on sample of Figure 30 compared with the high frequency ac conductivity measurements as a function of $1000/T^{\circ}K^{-1}$. Note the plateau in the dc values below 4.4 (above $-50^{\circ}C$).

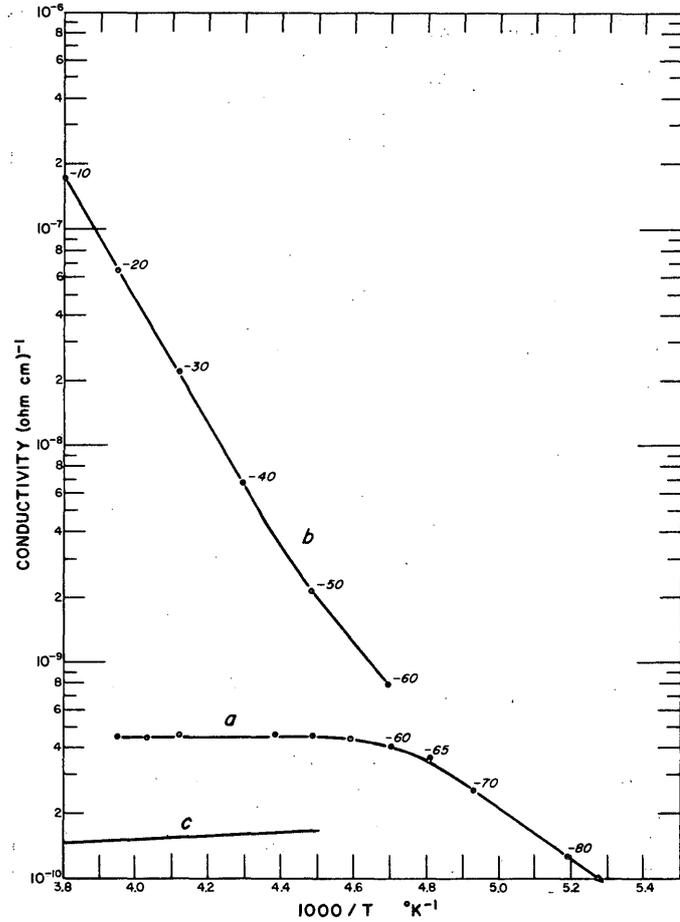


Figure 34. a. Four-probe dc conductivity measurements on a new sample prepared in the measuring cell of Figure 30 with even greater attention to purity than in that experiment. b. High frequency ac measurements on this sample. c. Four-probe dc conductivity data for sample grown in 3.2 cm diam measuring cell containing some demineralizer resin.

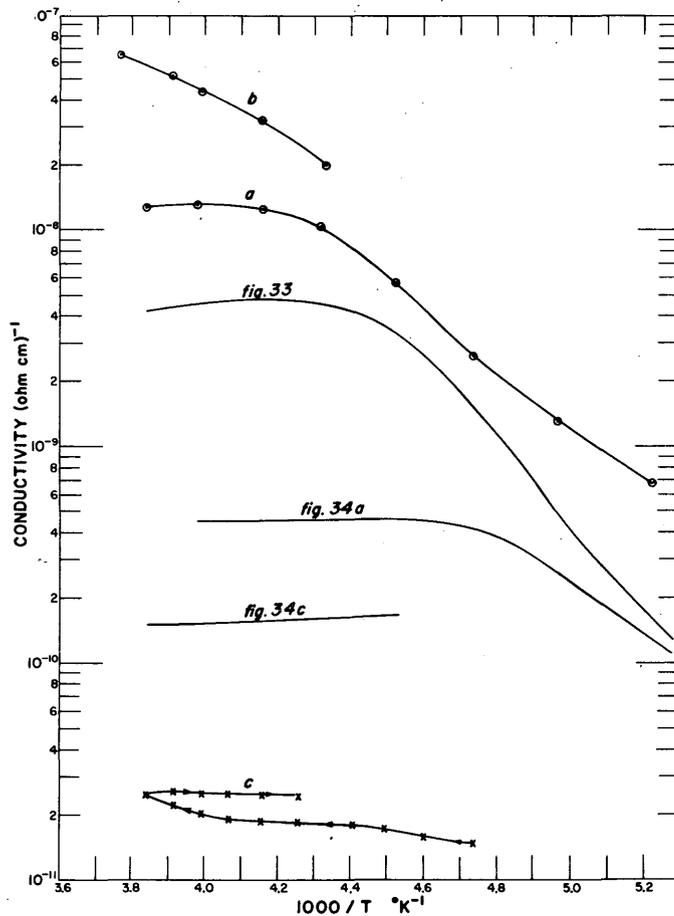


Figure 35. a. Four-probe dc conductivity data for a sample grown in the 1/8 in. diam measuring cell. b. Repeat of (a) after sample had been stored for 5 days at -20°C . c. Two-probe dc conductivity data for sample grown in the apparatus of Figure 29 (water continuously circulated through demineralizer). Arrows indicate sequence of measurements.

The dc conductivity of this sample as a function of $1000/T^{\circ}\text{K}$ is shown as curve c of Figure 34. It is seen that the conductivity is significantly lower than that of Figure 34(a) and that it has a $1/T^{\circ}\text{K}$ dependence down to -50°C . It is significant that this value is below that reported by Jaccard at -10°C [10^{-9} ($\text{ohm cm})^{-1}$] who also grew his samples in tubes containing demineralizer resin but who had to cut them and mount them between electrodes in order to measure them.

Still further sample purity was sought by constructing a new (two-electrode) apparatus which allowed the growing interface of the sample to be continuously flushed with 0°C water direct from the demineralizer (Section IV, Fig. 29). At 0°C the water measured 4×10^7 ohm-cm. The data are shown in Figure 35(c). The gradual rise as temperature is increased followed by the nearly constant values as temperature is again decreased are consistent with the hypothesis of a $1/T^{\circ}\text{K}$ temperature dependence and a gradual increase in conductivity with

time, becoming more rapid as temperature increases. This interpretation would indicate that the -10°C conductivity of the ice at the time of its formation was even smaller than $1.4 \times 10^{-11} (\text{ohm cm})^{-1}$.

For the sake of easy comparison, the dc data of Figures 33 and 34 have been replotted in Figure 35.

It is quite possible to prepare impure samples which have low dc conductances. However, in such cases we have always found that the conductance has an apparent activation energy. Figure 36 is a typical example. The sample was grown in a 0.6 cm diam polyethylene tube containing six platinum electrodes spaced 1 cm apart which divided it into five sections. The voltage across each of the three center sections (2, 3, 4) was measured while the end electrodes were used as current terminals. The bottom electrode was negative. The initial resistivity of the water was 2 megohm-cm. It is seen that although the conductivities are very low, they are strongly temperature dependent. Two of the three sections show similar behavior. The third is substantially different. This illustrates the variability which we always encountered when the water used was not of the highest purity. In this case no significant electrode polarization was observed at the current electrodes and reversal of the polarity of the applied voltage did not appreciably change the potential distribution. Substantial improvement in uniformity along a given sample can be achieved in small tubes such as this by agitation of the kind described in Section IV.

In view of the way dc conductance apparently disturbs the measurements of the high-frequency ac conductance (see Fig. 33) for those samples exhibiting a nearly temperature-independent conductance region, it is of interest to find out how the high-frequency ac conductance behaves for a sample which is impure but has a low dc conductance.

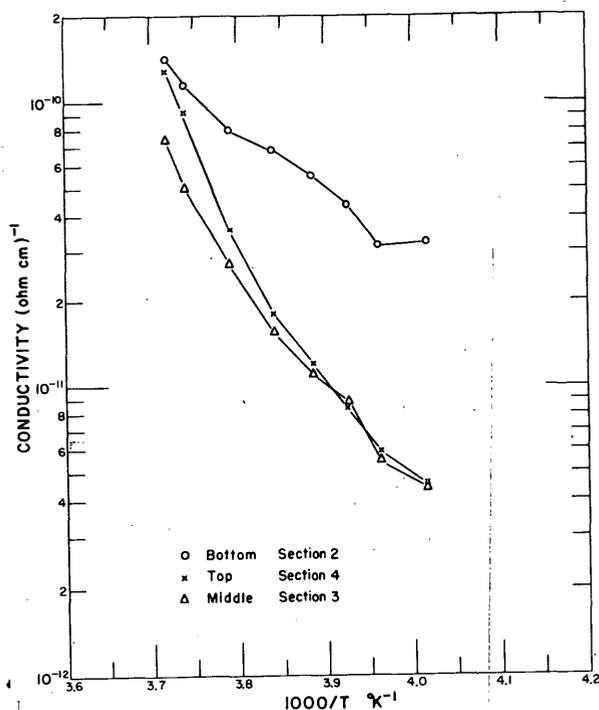


Figure 36. Six-probe dc conductivity data for sample grown from medium purity water (2×10^6 ohm-cm) in 0.6 cm diam polyethylene cell, showing the absence of the plateau and the variation of the data in successive regions along the sample.

Figure 37 shows the temperature dependence of the high frequency ac conductance for such a sample. It was prepared from 2 megohm-cm water in a six-probe 0.6 cm diam polyethylene tube, yet has a dc conductivity of $3.1 \times 10^{-10} (\text{ohm cm})^{-1}$ at -10°C . The high-frequency ac conductance appears to be undisturbed down to about -70°C . We believe this explains the fact that dielectric relaxation measurements such as those obtained by Cole fit very well an equation of the form $1/\tau = A e^{-E/RT}$ down to very low temperatures even though, by the present standards, the samples used seem impure. Because the ac conductivity is always well above the dc conductivity in the range of measurement, there is no problem.

Guarded electrode experiments

For reasons already mentioned, measurements made with guarded electrodes are more satisfactory than probe type measurements if polarization can be avoided. However, a guarded electrode structure is more complex than a simple probe device and this makes it difficult to arrange

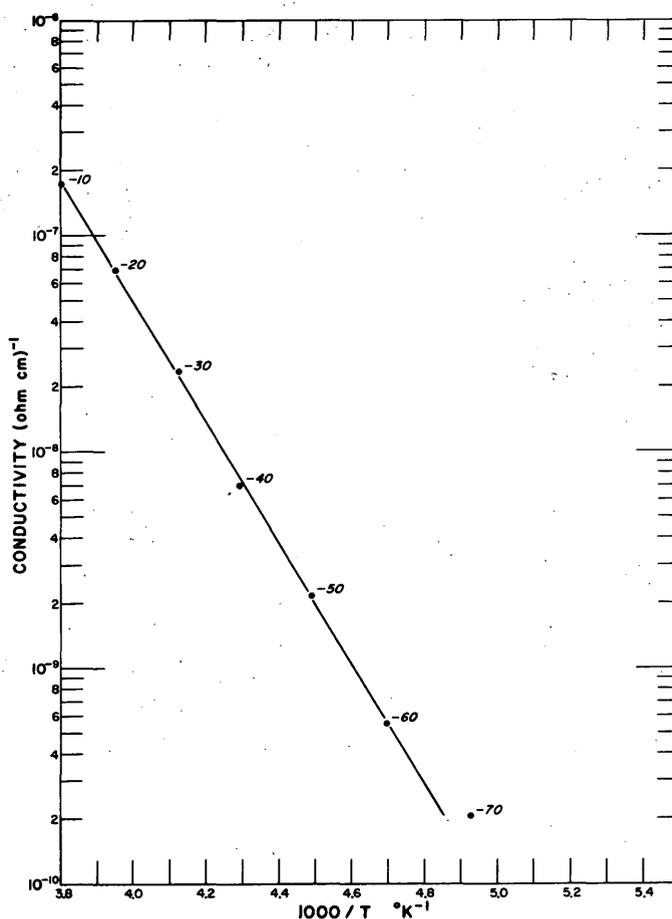


Figure 37. High frequency ac conductivity for a sample prepared in the same manner as that of Figure 36. Note that the ac data are undisturbed down to -70°C .

things so that the sample can be grown in the measurement cell. The situation becomes more difficult if one wishes to grow single crystals and still more difficult if the crystals are to be grown in running water or with ion exchange resin in the sample tube. Some possible techniques have been discussed. To date, our single crystal measurements have been confined to samples grown separately and then mounted in a guarded electrode apparatus. However, we have built an apparatus in which we expect to be able to grow single crystals between guarded electrodes. It has been used quite successfully for polycrystalline samples.

Single crystal, platinum plated electrodes. The observation that in very pure samples the dc conductivity was independent of temperature until the ac conductivity had dropped to about the same level as the dc value made it desirable to remeasure the single crystal sample 13 discussed in Section III. As mentioned, because of polarization, we were unable to obtain good dc data for this sample. However the ac conductance was measured as a function of frequency from -20°C to -90°C . At the higher temperatures, it proved possible to extrapolate the low frequency data to obtain an apparent dc conductance. The temperature dependence of the high frequency conductance and the low frequency conductance are plotted in Figure 38. The behavior is similar to that of the less pure multiprobe samples of Figure 35. Note, however, that this is extrapolated ac data, not dc data.

Platinum grid, guarded electrode. The problem of mounting a sample without contaminating it is only really solved if one grows the sample in the measuring apparatus. Thus a new guarded electrode system was built which would permit this to be done. The guard ring and electrodes were made of platinum screen. These were mounted in a Teflon tube (Fig. 39). The ends of the tube were sealed with Teflon plugs and O-rings making the system vacuum tight. The top plug contained built-in Teflon valves for filling and evacuating the tube. The lead wires (not shown) were of bare platinum and were brought out through small plugs in the end plugs. The system had an inside diameter of 2 1/4 in. and was 6 in. long. The grids were spaced 3/8 in. apart and the grid support structure was perforated so that ice could be grown up from the bottom through the grids into the top section. In this way the small sample measured would be grown from a large volume of water.

The apparatus was very carefully cleaned, and then leached for days in 18 megohm-cm water. Then 18 megohm-cm water was run through it for a few minutes before it was sealed. Ice was frozen up from the bottom by lowering the apparatus slowly into a cold bath (-25C). The ice which grew was later found to be clear and polycrystalline. It was composed of large columnar grains whose axes were roughly parallel to the c axis and perpendicular to the electrodes. The data for this sample are plotted in Figure 40. Measurements were only continued to -40C but they show clearly the pattern of behavior found for the other very pure samples.

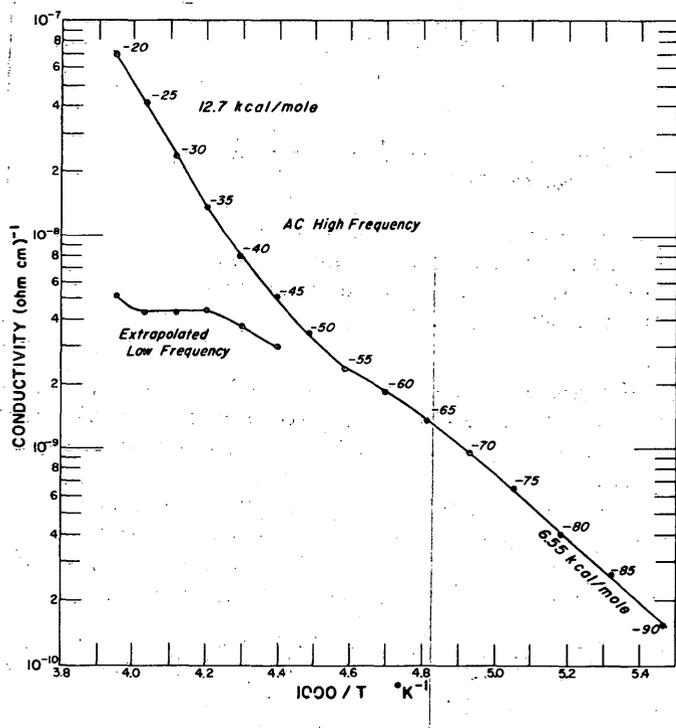


Figure 38. High frequency ac conductivity data and extrapolated low frequency ac data for single crystal sample 13. These measurements were made prior to the dc measurements of Fig. 24.

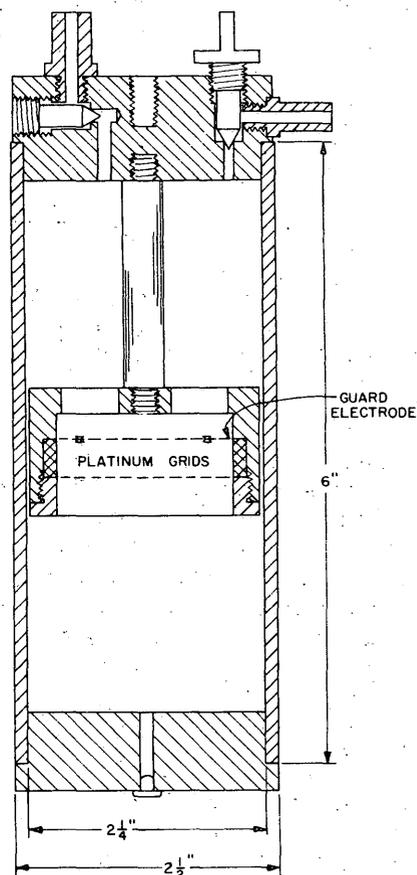


Figure 39. Apparatus for growing a sample in a sealed guarded ring measuring assembly.

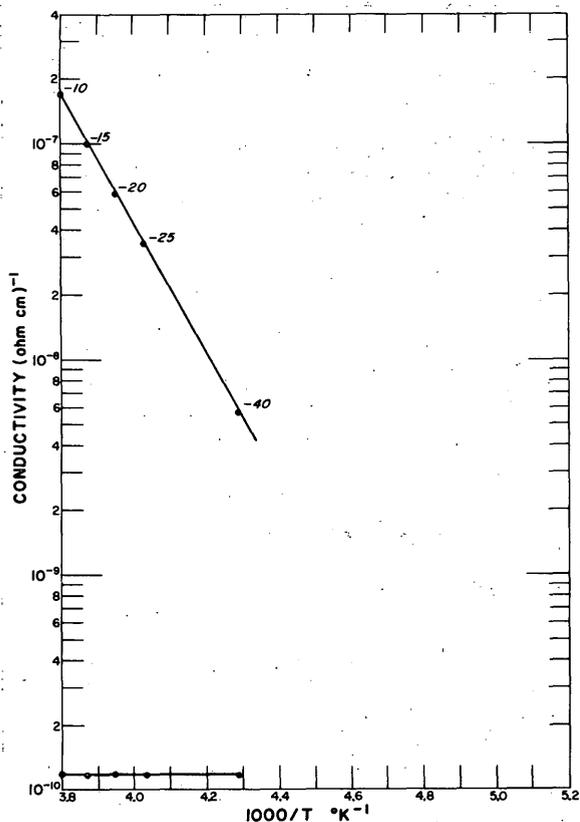


Figure 40. Two-probe dc and high frequency ac data for a high purity sample grown in the apparatus of Figure 39.

at different values for different samples. For some samples it is as high as 10^{-8} (ohm cm) $^{-1}$ and for others as low as 2×10^{-11} (ohm cm) $^{-1}$. (Values of the order of 10^{-9} (ohm cm) $^{-1}$ are commonly reported at -10°C for the temperature dependent conductivity measured in other laboratories.)

Samples which we believe to be relatively impure (from the conductivity of the water and the manner of preparation) show very strongly temperature dependent dc conductivity and "normal" ac conductivity. However, the dc conductivity of impure samples and its temperature dependence are not only different from sample to sample but are different from section to section on the same sample. We have measured apparent bulk activation energies of from 5 to 13 kcal/mole.

We have searched in vain for a means of explaining the conductivity plateau as an artifact of experiment. For example, if the ice broke away from the electrodes a high, temperature-independent series resistance would be introduced into the system. However, if this happened at the current electrodes it would not affect the conductivity measurement in a multiprobe experiment. It would merely appear as an anomalously high electrode potential drop similar to that caused by electrode polarization. External conducting paths due to frost or other causes would cause an apparent conductivity minimum rather than a maximum. The very number of different current values at which the plateau occurs, the fact that a given value changes with time, the break in the ac conductivity curve and the way the data all appear as part of a set all argue strongly against the possibility of an

From these experiments, it appears that when very pure samples are prepared the dc conductivity is nearly independent of temperature over a considerable range, the extent of the range increasing and the magnitude of the conductivity decreasing with the purity of the sample. These samples show time independent currents, absence of electrode polarization, and nearly identical behavior from section to section in the multiprobe apparatus. Coupled with this unique dc behavior is an ac conductivity (frequency much higher than the dispersion frequency) which behaves "normally" in the region for which the dc conductivity is temperature independent in that it decreases with decreasing temperature exhibiting an activation energy of about 13 kcal/mole. However, when the ac conductivity falls to the same magnitude as the dc conductivity, there is a break in the temperature dependence curves and the ac conductivity falls very much more slowly with decreasing temperature. At the same temperature the dc conductivity begins to drop with decreasing temperature.

This behavior apparently deteriorates with time. That is, the dc conductivity gradually increases and becomes temperature dependent. The rate at which this deterioration takes place increases with increasing temperature. We find that the plateau in dc conductivity occurs

instrumental malfunction. Thus we seem forced to accept these data as describing a real property of ice, at least of ice prepared in this way and measured shortly after preparation. (We should note that Jaccard, Siksna, and Heinmets all made a point of annealing their samples for a matter of days before making their measurements.)

The symmetry of the ac and dc results immediately suggests that there are fundamental processes which contribute to the ac conductivity in parallel and to the dc conductivity in series. Two possible electrical analogues are shown in Figure 41 together with their dc and ac equivalents. Thus for instance we would have for Figure 41a

$$\left. \begin{aligned} \sigma_{ac} &= \sigma_1 + \sigma_2 \\ \sigma_{dc} &= \sigma_1 \sigma_2 / (\sigma_1 + \sigma_2) \end{aligned} \right\} \quad (21)$$

and $\sigma_{ac} \sigma_{dc} = \sigma_1 \sigma_2$

Let $\sigma_1 > \sigma_2$ at high temperatures and $\sigma_1 < \sigma_2$ at low temperatures. Then

High temp $\sigma_{ac} \sim \sigma_1$

Low temp $\sigma_{ac} \sim \sigma_2$

$\sigma_{dc} \sim \sigma_2$

$\sigma_{dc} \sim \sigma_1$

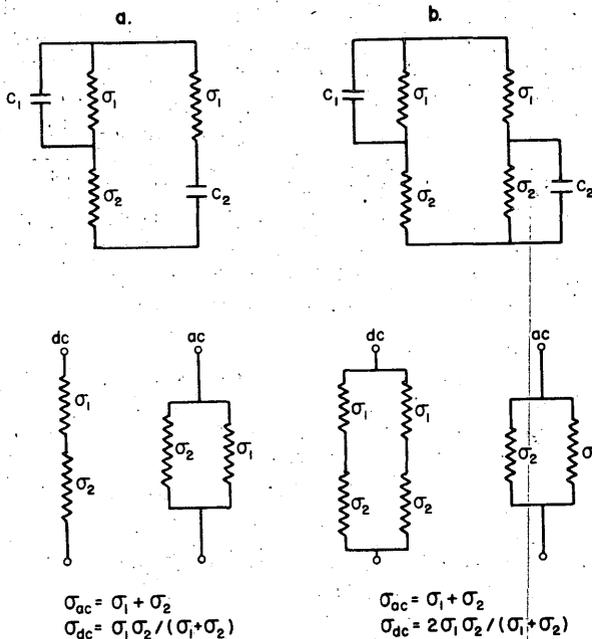


Figure 41. Possible electrical analogues of samples which exhibit a plateau in dc conductivity and a break in ac conductivity as in Figure 33.

An interpretation of this kind is strengthened further if we plot the $\log \sigma_1 \sigma_2$ as a function of $(\text{temperature})^{-1}$. This is done in Figure 42 for the data of Figure 33. The result is very nearly a straight line over the whole temperature range -10C to -90C . This is just what we would expect if σ_2 were nearly temperature independent and σ_1 obeyed the Arrhenius equation. It is very tempting to use the conduction model of Granicher et al. and ascribe σ_1 to the rotation of dipoles and σ_2 to the translation of ions. This would imply that in our plateau-producing samples a constant number of ions, independent of temperature, was available for conduction and that this number differed from sample to sample as a result of impurity content or defect structures. Thus in the purest ice the ionic conductivity would be less than the lowest we have measured, $2 \times 10^{-11} (\text{ohm cm})^{-1}$, and would occur by ion tunnelling, being ion limited at high temperatures and rotation (Bjerrum defect) limited at low temperatures. Why the ion concentration might be independent of temperature we cannot say. Possibly a trapping mechanism is operative.

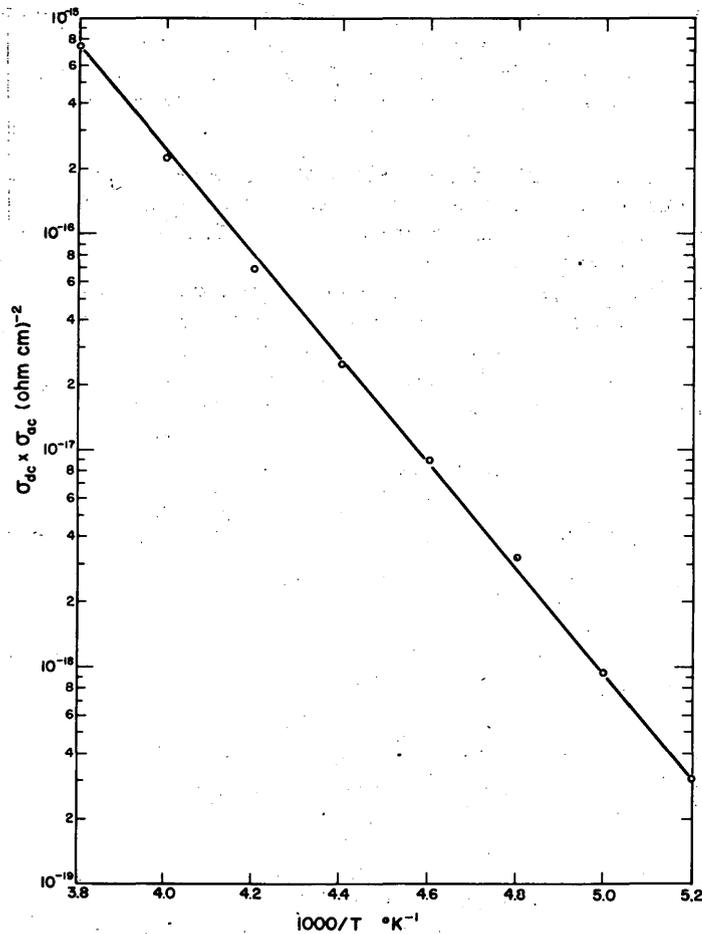


Figure 42. Semi-log plot of the product $\sigma_{ac}\sigma_{dc}$ as a function of $1000/T^{\circ}\text{K}^{-1}$ for the data of Figure 33.

VI. CONCLUSIONS

Many determinations of the dc electrical conductivity of ice have been made at different laboratories in various parts of the world. The results are most unsatisfactory for there is no unanimity as to its value. Activation energies for conduction of from 6 to 24 kcal/mole have been proposed. In the introduction, it was suggested that this great disparity might arise from sample contamination on the one hand and surface conductivity on the other. That surface conduction can play an important role seems to have been demonstrated by the slim rod experiments of Section III. However, the situation is more complicated than we had first supposed. In order to justify the numbers which we obtained, large values of conductivity, together with large apparent activation energies, we have been forced to postulate a surface conduction region whose effective thickness varies with temperature. This model agrees qualitatively with the picture of a disordered surface region of temperature-dependent thickness which has been suggested by others in

accounting for interfacial viscosity, regelation and other remarkable properties of ice. By a suitable choice of undetermined constants, the agreement can be made semi-quantitative. As might be expected, the conducting properties of this region appear to be quite strongly modified by slight amounts of impurity. Nonetheless they are surprisingly stable, indicating that the state of contamination is also quite stable.

The guard ring experiments were originally intended as surface experiments. However, the dc measurements were too erratic to be useful. We believe this to have been largely the result of electrode effects. The ac measurements, for which polarization was not a problem, were satisfactory. With this geometry, the surface to volume ratio was reduced so much in comparison to the slim rod experiments that the surface contribution was largely masked by the bulk properties. The differences between the characteristics measured for the outer zone and those for the inner zone are believed to result largely from a slightly higher concentration of impurities in the outer portions of the sample. This is consistent with the observations (Camp, 1963, p. 3) that the impurity concentration of doped ice crystals is greatest near the walls of the container in which they are frozen.*

The guard ring experiments also established that a free surface adjacent to an ice-electrode system was helpful in reducing polarization effects and that grain boundaries or a Lucite jacket surrounding the sample had little effect on the ac properties which were measured.

Because it became increasingly clear as experiments progressed that techniques of moderate purity were not satisfactory, a systematic attempt was made to reduce sample contamination. Efforts also were made to reduce electrode polarization. Water of very high purity was obtained by distillation and subsequent ion exchange. Its purity was maintained by keeping out soluble gases, using very carefully cleaned Teflon sample tubes and clean platinum electrodes. It was found that the use of platinum electrodes as opposed to gold, aluminum, rhodium, or copper reduced electrode polarization. Moreover, it seemed to be reduced also by improving the purity of the water. Rhodium electrodes were second to platinum. Palladium, which has been reported to have excellent properties in this respect, was not used. The sample which we believe to have been purest was grown in water which was constantly being recirculated through ion exchange resin.

Under conditions of high purity, we found that the dc conductivity of freshly grown samples was nearly constant over a wide range of temperature. It dropped only as the temperature became so low that the high frequency ac conductivity approached the dc value. At temperatures higher than this the ac conductivity decreased with decreasing temperature in a "normal" way, falling exponentially in $1/T^\circ K^{-1}$ with an activation energy of about 13 kcal/mole. At lower temperatures the dc conductivity fell rapidly and the ac conductivity fell much more slowly. However, these decays occurred in such a way that $\log(\sigma_{ac}\sigma_{dc})$ plotted against $1/T^\circ K^{-1}$ gave almost a straight line over the whole range of temperature. The behavior was very much as if the dc conductivity resulted from two processes in series and the ac conductivity resulted from the same two processes in parallel.

The behavior was observed only during the first few days after a sample had been prepared. At temperatures close to 0C, the plateau in conductivity was

*While this report was in preparation Professor N. Riehl of the Technische Hochschule, Munich, visited USA CRREL and told us of the work at his laboratory on the distribution of impurities in doped ice (Blicks, Egger and Riehl, Phys. Kondens. Materie, vol. 2, p. 419, 1964). They have correlated the impurity distribution with the abundance of defects in the lattice. These they have found to be greatest near the surface where they are presumed to result from the difference in thermal expansion between the ice and the material of the tube in which it is grown.

observed to rise with time. At present we cannot account for this behavior other than to suggest that it might result from ion producing impurities diffusing in from the surface or from the annealing out of ion traps. The extent to which a plateau was obtained and the value of conductivity at which it appeared seemed to be directly related to the purity of the sample. The results from what we believe to have been our most carefully prepared sample indicate that the conductivity for the purest ice before it is annealed is less than 1.4×10^{-11} (ohm cm)⁻¹ and is nearly independent of temperature (possibly going as 1/T) down to -60C or below. The possibility of an unsuspected impurity being contributed by the ion exchange resin must not be overlooked.

Experiments with samples of less than the highest purity always showed a sharply decreasing conductivity as temperature was reduced. However, these measurements indicated a wide variety of activation energies for dc conduction as well as for actual conductivity values. In none of these cases did the high frequency ac conductivity seem to be disturbed. But here because of the decay of dc conductivity with temperature, the ac conductivity was always substantially higher than the dc value.

As yet, we have no really satisfactory interpretation of the conductivity plateau and its time dependence. However, we believe that its appearance and the experiments leading up to its discovery are ample evidence that one must regard with skepticism all statements to date about the magnitude of the dc conductivity of pure ice.

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APPENDIX A. CALCULATION OF MAXIMUM CONDUCTIVITY

For a conduction model based on rather general and physically reasonable assumptions, we show that there is a maximum possible conductivity σ_{\max} . In the case of an exponential temperature dependence, it is shown that at any given temperature the value of $\log \sigma_{\max}$ is proportional to the negative of the activation energy for conduction.

Assumptions:

1. The current is carried by mobile charges q , which may be present as a result of thermal ionization of water or impurity molecules, the activation energy for ionization being ϵ_i .*
2. The transport of charge takes place by jumps between adjacent lattice sites separated by a distance λ . Each jump requires the traverse of a potential energy barrier ϵ_μ .
3. Only one type of charge carrier is important (only one sign).

Define:

n_s = number of ionizable surface molecules per square centimeter of surface.

n = number of ionizable molecules per cubic centimeter.

m_s = number of mobile ions present per square centimeter of surface.

m = number of mobile ions present per cubic centimeter.

E = electric field strength, volts/cm

σ = conductivity, (ohm cm)⁻¹

σ_s = surface conductivity, (ohm)⁻¹

μ = charge mobility, cm²/volt-sec

k = Boltzmann's constant

T = Kelvin temperature

ν = number of times per second a charge jumps the barrier between two stable positions.

The basic argument is that since

$$\sigma = m q \mu \tag{A1}$$

*Because of the possible confusion which may arise between E , the electric field strength and ϵ , the activation energy in kcal/mole for a rate limiting process (cf. eq A10) we use the symbol ϵ with an appropriate subscript for the activation energy per particle for a rate limiting process. (There will be no confusion here with ϵ as used earlier to indicate dielectric constant.) Thus in Appendix A $N_0 \epsilon = E$ and $\exp(-\epsilon/kT) = \exp(-E/RT)$ where N_0 = Avogadro's number.

and since m , q , and μ all have physically reasonable upper bounds, σ must be bounded. If m and μ are temperature dependent then the upper bound on σ must also be temperature dependent. We show this in more detail below.

$$m = n e^{-\epsilon_i/2kT} \quad (A2)$$

by the law of mass action.

Since mobility is the velocity v per unit field

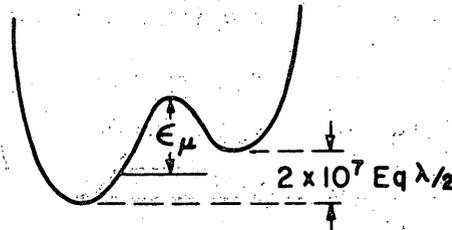
$$\mu = v/E = \lambda v/E: \quad (A3)$$

We have assumed that the jumps take place between adjacent potential minima separated by a barrier ϵ_μ . When no field is applied, the number of jumps per second to the left equals that to the right.

$$v_{21} = v_0 e^{-\epsilon_\mu/kT} = v_{12} \quad (A4)$$

where v is an appropriate frequency factor which can not be greater than the lattice frequency.

When a field is applied, we lower the potential well on one side of the barrier and raise it on the other by an amount $10^7 E q \lambda/2$ ergs. Then the frequency of jumps to the right, v_{12} , is less than the frequency of jumps to the left, v_{21} .



$$v_{21} - v_{12} = v_0 e^{-\epsilon_\mu/kT} \left(e^{10^7 E q \lambda / 2kT} - e^{-10^7 E q \lambda / 2kT} \right) \quad (A5)$$

or since $10^7 E q \lambda \ll kT$

$$v_{21} - v_{12} = v_0 e^{-\epsilon_\mu/kT} 10^7 E q \lambda / kT. \quad (A6)$$

Thus

$$\mu = 10^7 \frac{\lambda^2 q}{kT} v_0 e^{-\epsilon_\mu/kT} \quad (A7)$$

and

$$\sigma = 10^7 \frac{\lambda^2 q^2}{kT} n v_0 e^{-(\epsilon_i/2 + \epsilon_\mu)/kT}. \quad (A8)$$

Defining $\epsilon_{\sigma} \equiv \epsilon_i/2 + \epsilon_{\mu}$ we have for bulk conductance

$$\sigma = 10^7 \frac{\lambda^2 q^2}{kT} n \nu_0 e^{-\epsilon_{\sigma}/kT} \quad \text{Bulk (A9)}$$

For surface conductance we will have

$$\sigma_s = 10^7 \frac{\lambda^2 q^2}{kT} n_s \nu_0 e^{-\epsilon_{\sigma_s}/kT} \quad \text{Surface (A10)}$$

Now q cannot reasonably be larger than the electronic charge, λ cannot be larger than the intermolecular distance, n cannot be larger than the number of water molecules per cm^3 , and ν cannot exceed the lattice frequency. Substituting these values

$$q = 1.6 \times 10^{-19} \text{ coulomb}$$

$$\lambda = 2.76 \times 10^{-8} \text{ (this really assumes a jump plus a rotation of a molecule)}$$

$$n = 3.3 \times 10^{22} \text{ per cm}^3$$

$$n_s = 10^{15} \text{ per cm}^2$$

$$k = 1.38 \times 10^{-16} \text{ erg/}^\circ\text{K}$$

$$\nu = 3 \times 10^{13} \text{ sec}^{-1}$$

$$\text{Max } \sigma = 4.23 \times 10^{-17} \frac{n}{T} e^{-\epsilon_{\sigma}/kT} = a_{\text{max}} e^{-E_{\sigma}/RT} \quad \text{Bulk (A11)}$$

$$\text{Max } \sigma_s = 4.23 \times 10^{-17} \frac{n_s}{T} e^{-\epsilon_{\sigma_s}/kT} \quad \text{Surface (A12)}$$

at -10C we have

$$\text{Max } \sigma = 5.3 \times 10^3 e^{-1.9E_{\sigma}} \quad \text{(A13)}$$

where $E_{\sigma} = N_0 \epsilon_{\sigma} \text{ kcal/mole}$

$$\text{Max } \sigma_s = 1.6 \times 10^{-4} e^{-1.9E_{\sigma_s}} \quad \text{(A14)}$$

where $E_{\sigma_s} = N_0 \epsilon_s \text{ kcal/mole}$

or

$$\text{Max log}_{10} \sigma = 3.725 - 0.825 E_{\sigma} \quad \text{(A15)}$$

$$\text{Max log}_{10} \sigma_s = -3.795 - 0.825 E_{\sigma_s} \quad \text{(A16)}$$

Typical values are given in Table AI.

Table AI. Maximum values possible for bulk and surface conductivity at -10°C.

Activation energy (kcal/mole)	σ_{max} (bulk) (ohm cm) ⁻¹	σ_{s} max (surface) (ohm ⁻¹)
1	8×10^2	2.4×10^{-5}
5	4×10^{-1}	1.2×10^{-8}
10	3.0×10^{-5}	9×10^{-13}
13	1×10^{-7}	3.1×10^{-15}
19	1.1×10^{-12}	3.2×10^{-20}
24	8.4×10^{-17}	2.5×10^{-24}

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13. ABSTRACT In an attempt to resolve the conflict existing in the literature as to dc electrical conductivity of ice, an extensive series of measurements has been made. Since surface conduction is a possible cause of some of the confusion, both bulk and surface conductivity have been measured at dc and audio-frequencies. Evidence was found for significant surface conductivity when slight contamination was present. In order to explain these results quantitatively, it is necessary to postulate a surface conduction region whose thickness varies with temperature. Extrinsic bulk conductivity due to trace impurities has been found to play an important part also and probably accounts for some of the disagreement in the literature. Using ice of the highest purity, bulk measurements show that, for a fresh sample, the dc conductivity is nearly independent of temperature down to temperatures at which the high frequency ac and dc conductivities are about equal. The results suggest that the high frequency conductivity is limited by 2 processes in parallel and that the dc conductivity is limited by the same 2 processes in series.			

14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

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ROLE

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Ice--Conductivity
Ice--Electrical properties--Temperature factors
Ice--Impurities--Electrical properties
Ice--Surface properties
Ice--Thermoelectric effects
Ice--Testing equipment