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DIELECTRIC PROPERTIES OF STRAINED ICE. II : EFFECT OF SAMPLE PREPARATION METHOD

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Résumé. La préparation d'échantillons de glace utilisés dans la mesure des propriétés diélectriques induit trop souvent d'importants effets mécaniques. Ces effets ont été étudiés par comparaison avec des mesures réalisées avec des échantillons obtenus sans effets mécaniques importants.

Abstract. Since most commonly used sample preparation methods for ice dielectric studies involve rather heavy mechanical straining, the effects of straining were studied and compared with more strain-free sample preparation methods.

1. Introduction

As discussed in an accompanying paper, the dielectric properties of ice can be modified drastically by straining, probably through the modification of dislocation structures. Most methods customarily used in sample preparation for dielectric studies involve mechanical cutting or grinding, or freezing of the samples between the electrodes. It is obvious that such treatment can distort the crystals, making the dielectric properties different from the as-grown state. In the case of samples grown between electrodes, mechanical strain could arise due to the difference in thermal expansion coefficients. Auty and Cole (1) reported cracking between electrodes and ice upon cooling to below -40°C.

During the course of our dielectric studies we also encountered several anomalous phenomena which may have been caused by mechanical straining in the crystals. In this paper we describe the effects of various sample preparation methods.

2. Sample Preparation Methods and Results

Freezing in situ between electrodes

Freezing of ice samples between electrodes was the preparation method used in most early studies (1). Electrode System C (described in Part I) was slightly modified to allow freezing of in situ crystals. A set of spacers were inserted in the guard ring area between the high and low electrodes. The electrodes were wrapped in polyurethane film, and distilled and deionized water was introduced between them. The ice growth methods included very slow ice growth at a cold-room temperature of -1°C as well as rapid growth induced by filling the gap between the electrodes and a seed crystal with distilled and deionized water at -10°C.

For the slowly grown ice, very strong negative conductance disappeared in 4 days at -29°C and never reappeared. An interesting observation is that relaxation at the higher frequency range was very close to the Debye type. Its closeness can be judged by the straightness of the capacitance vs conductance plot and also by the ratio of relaxation time, the "Debye index," shown on Line 2 of the tabulated data on the results sheet in the accompanying paper. This ratio, which should be 1 for the case of pure Debye relaxation, was 0.88 or higher over more than one decade and remained this way. This was the closest to the Debye type during the course of our studies. The sample was lost when it was being dismounted from the electrodes so that we were unable to determine the orientation. But the lower frequency "tail" of this particular sample was very short, suggesting that the major part of the crystal was oriented with considerable deviation from C-axis parallel.
Compared with this slowly grown sample, rapidly grown samples show considerable deviation from Debye relaxation. Samples with seeds having C-axes oriented parallel to the electric field had large lower frequency tails, and the transition between high and low frequency relaxation was sometimes obscured. In contrast, crystals grown with C-axes perpendicular to the electric field had very small low-frequency tails and relaxation was closer to the Debye type.

**Samples frozen onto electrodes**

One side of a 45-degree-cut crystal slab sample was slightly melted with a warm metal surface, and quickly frozen onto a cold electrode surface at -10°C. The other side of the sample was treated in the same way.

A very long tail was observed on the low-frequency side of a Cole-Cole plot made immediately after sample preparation, as shown in Figure 1 (designated -9.3/0 hr). On warming up to -1.1°C, the tail shifted toward the negative side of $\varepsilon'$ (designated -1.1/14 hr) but shifted back to the positive side following slight cooling (-4.3/28 hr). On slight warming of 0.7°C, the slope again shifted to negative (-3.6/122 hr). At a much lower temperature of -22.8°C the Cole-Cole plot appears perfectly normal (-22.8/165 hr) but it returned to negative by warming up to -1.4°C. As annealing proceeded, a stronger negative trend seemed to emerge (-3/254 hr). The GR 1615 capacitance bridge is capable of switching both the conductance standard and capacitance to the sample side of the bridge. Balancing the bridge by connecting the internal capacitance parallel to the sample means negative capacitance of the sample. Since only the temperatures of the sample, the electrode and a short length of cable were varied, the source of such negative capacitance must be within this system. Quite possibly the ice sample is the source of this anomaly.
During studies of the internal field by charged dislocation using a computer model, we observed negative capacitance behaving in a similar manner. Beyond a certain limit of dislocation density, the internal field effect can feed back to the dislocation motion, causing catastrophic behavior similar to the Mossotti catastrophe. With distributed relaxation time such catastrophic behavior appears in the lower frequency range as observed here.

**Warm die-drawn samples**

All samples used in the straining experiments were prepared by warm die-drawing methods. Also, one series of experiments were conducted without straining. This method is preferred to the others, since it easily produces samples of uniform size with a minimum of induced strain. Stacking faults may be generated in the course of the drawing, but will be eliminated in about 12 days at -20°C so that a few days of annealing near 0°C will suffice to clear the stacking faults (2).

The general features of the results using warm die-drawn crystals lie between those of slow freezing, showing nearly pure Debye type relaxation, and those of crushed ice, having a widely distributed relaxation time. Samples oriented in an electric field at 90 and 45 degrees with respect to the C-axis tended to have shorter low-frequency tails. Longer tails were shrunk quickly to a minimum by annealing. Contrarily, crystals cut so as to have their C-axes parallel to the electric field showed very large low-frequency tails.

![Cole-Cole plot](image)

Fig. 2. Strong negative conductance gradually decreased and became positive.

One of the C 45-degree cut samples showed strong negative conductance, extending the Cole-Cole plot to the negative side of the k'-k" plane, as shown in Figure 2. This negative conductance gradually diminished as the straining progressed and the sample eventually showed normal behavior. Attempts to reproduce such persistent negative conductance samples have failed, though short-lasting negative tails have been observed frequently.

**Alcohol-polished samples**

Both sides of a C 45-degree cut sample were polished using a polishing cloth impregnated with a 40% alcohol, 60% water solution (Buehler Microcloth) and a holder similar to that described by Takei and Maeno (3). About 1 mm was removed from each side of the bandsaw-cut sample.

Interestingly, the Debye index remained relatively low (0.7 to 0.9). Relaxation strength started low (40) and went up to 80 after slight straining. Lower relaxation strength was expected for this sample since dislocation density would be low with little straining.

**Sanded samples**

Sanding was used to make flat surfaces in studies by vonHippel et al. (4). In our studies a sample was oriented and cut by a bandsaw so its C-axis was perpendicular to the electric field. The sample was first microtomed to form a slab about 6 mm thick and then both surfaces were sanded with #220 sandpaper. The Cole-Cole plot was rather flat, but the Debye index had a relatively high value of 0.85 to 0.9. Relaxation strength was generally 90 to 100, considerably greater
than the strain-free samples prepared using the alcohol polishing or die-drawing methods but comparable to the plastically strained samples discussed in the accompanying paper.

**Crushed single-crystal samples**

A piece of single-crystal ice was crushed between 4.05-cm-diameter anvils at 15 MPa in a vacuum. A central piece was cut and again compressed between the anvils at 21 MPa to make a 4.8-mm-thick disk. The sample was chilled to -62°C in a cold box prior to preparation, and immediately after it was made and mounted between electrodes it was placed back in the cold box to prevent recrystallization.

We started with very pure ice and crushed it in a vacuum to make a solid column of ice. So although the sample produced was very fine-grained its extensive grain boundary surface ran little risk of being exposed to contamination. Also, we started at a lower temperature so that residual stress would remain high. A large deviation from Debye relaxation, as would be expected, was observed even after 2 weeks of annealing above -5°C. Most of the stress should have been relaxed, and considerable grain growth took place within this annealing time; grain boundary conduction would be the major source of deviation after annealing.

**Dislocation-free sample**

The dielectric properties of dislocation-free areas of hoarfrost crystals were measured using electrode System A (micro-mercury electrodes). As discussed previously, very small dielectric relaxation was observed at about one-tenth of the normally observed relaxation time. The relaxation strength and time were changed to near normal by scratching the crystal surface with the tip of a hypodermic needle. A detailed discussion of this has already been published (5); no further discussion will be given.

3. Discussion

Complex behavior was observed in connection with the various single-crystal sample preparation methods. Though dispersion seemed close to the Debye type, the observed Debye index [ratio of relaxation times \( R_{4}(k'' \times \omega)/R_{4}(k''/\omega) \)] was generally low (0.7-0.9), and the frequency range required to produce a ratio larger than 0.8 seldom covered more than one decade.

Relaxation closest to the Debye type was observed in the samples frozen slowly between the electrodes, even though lower frequency conductance showed a strong negative trend at the beginning of the series of measurements. This was not a single crystal but a coarse-grained polycrystal sample, however. When the seed crystal filled the space between the electrodes, the results we observed constituted mostly the seed crystal, but air gap effects should be absent.

Polycrystalline ice made by crushing single crystals between anvils produced a heavily skewed Cole-Cole semicircle and a broad relaxation peak at -40°C. After prolonged annealing above -5°C for over 10 days, a slightly flatter Cole-Cole semicircle with a large tail developed. However, the relaxation peak remained broad. Considerable flattening of the Cole-Cole semicircle at lower temperature was observed in the second cooling-warming cycle after annealing.

Computer model studies of air gap and film material effects on purely Debye dispersion materials indicated that the Debye index was larger than 0.85 and covered at least one decade of frequency range unless the air gap was very wide (0.5 mm) on the model. Also, the \( k' \) vs \( k'' \times \omega \) plot on the computer model has a long, straight portion, unlike the real crystal. On the real crystal the \( k' \) vs \( k'' \times \omega \) plot was never straight, indicating that the relaxation spectra were generally spread, and real Debye relaxation was seldom observed in the extended frequency range.

As discussed in the accompanying paper, dielectric dispersion can be modified considerably by plastic deformation. Moreover, the dielectric dispersion observed on dislocation-free ice was very small, indicating the strong effects of dislocations on the dielectric properties of ice.

Part of the observed behavior could be explained by point defect theory. An increase in relaxation strength could be caused by an increase in point defects. However, the same theory would have to explain the increase in relaxation time. And it should be able to describe the distributed dispersion and negative conductance and capacitance. (Or, alternatively, a separate theory would have to be developed.)
Many of the observed properties, including the linear relationship between dielectric relaxation time and strength and the distribution of relaxation time, can be easily explained by charged dislocation theory. Also, some anomalies observed during this study, such as negative conductance, negative capacitance, and occasional sudden disturbances in bridge balancing, might possibly be explained by charged dislocation theory.

References


COMMENTS

G.W. GROSS

Have you considered electrode polarization as a possible reason for "negative electrical conductivity"?

Answer:

I had not taken into account any electrode polarization here, but I feel it may appear out side of my measurements.