

Electrical effects during condensation and phase transitions of ice^{a)}

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Condensation potentials and corresponding electrical currents are observed during the isothermal growth of amorphous, cubic, and hexagonal ice from the vapor phase. Upon heating of the condensate a thermally stimulated current (TSC) spectrum is observed with the application of any external electric field. Current peaks in the TSC spectrum are shown to be of two types: depolarization currents related to dipolar relaxation processes in the condensate and peaks due to phase transitions. Nearly all depolarization (~90%) occurs in the amorphous phase via relaxation processes. Shifts in the maximum temperature of the peaks are observed for deuterated water for both types of peaks, and are on the order of 5–10 K. Models are proposed for the electrical effects observed during condensation, phase change, and depolarization.

INTRODUCTION

Water has attracted the attention of scientists since ancient times.¹ The structure of solid water, however, has been studied only since the nineteenth century. Since then more than 10 different crystalline forms of ice have been described and investigated by various means such as dilatometric techniques, differential thermal analysis, x-ray and neutron diffraction, calorimetry, and thermal conductivity.² The structure of liquid water, on the other hand, has been the subject of detailed investigations only during the present century, when special techniques such as neutron diffraction could be used. Of course, the understanding of liquid water is of paramount importance in biology and chemistry.^{3,4} The interaction of water, in a possibly structured form, with biopolymers and other materials and electrical effects associated with it have been reported.⁵ In 1935 an amorphous form of solid water was found by Burton and Oliver.⁶ It has since been confirmed by others with neutron and x-ray diffraction, infrared absorption, density measurements, reflectometry, differential thermal analysis, and Mossbauer effect experiments.⁷ More recently, Rice and collaborators,⁸ using neutron and x-ray diffraction and Raman scattering, reported seeing two amorphous phases: a high density form, appearing in condensates formed at very low temperatures (10 K), as well as the low density form previously found by condensation at liquid nitrogen temperature. It is also known² that amorphous films crystallize upon heating, first into a cubic form at ~150 K and then into a hexagonal form at ~200 K. In this way a most complex picture emerges for the physical behavior of the structure of water ranging from

many crystalline phases, to one or two amorphous phases, and a liquid phase with many changing properties. As concerns electrical transport processes, ice was shown to be a protonic semiconductor.⁹ Extensive literature exists in this area.²

Since the work that we report here concerns some electrical effects in ice, let us first review this area. Costa Ribeiro in 1943¹⁰ discovered an effect related to the appearance of potentials and electrical currents during solidification of many substances including water. This was also confirmed later by Workman and Reynolds who used different water solutions and found freezing potentials to be impurity dependent.¹¹ Since the effect might be important for the explanation of atmospheric electricity, these studies have stimulated the interest of many investigators.¹² Pinatti and Mascarenhas¹³ undertook one of the first quantitative studies of the Costa Ribeiro effect in the water-ice system under controlled conditions of phase change also using single-crystalline samples. The B. Gross model¹⁴ for the Costa Ribeiro effect was shown to be a proper framework for understanding the general properties of the effect. More recent work of B. Gross¹⁵ and others has brought the study of freezing potentials in different solutions to a more quantitative basis. Besides the Costa Ribeiro Effect two other phenomena should be mentioned here, related to electrical properties of ice. The first is the existence of the ice electret; the second is the possible ferroelectricity of ice. The possibility of charge and polarization storage in ice via the electret state by the application of an external electric field was first found independently by several authors.¹⁶ Arguello and Mascarenhas¹⁷ showed that the electret effect in ice was strongly dependent on hydrogen fluoride doping and that besides the postulated dipolar mechanism a strong space charge component was present and was related to the transport properties of the lattice defects in ice. They used the thermally stimulated current (TSC) technique to investigate the charge and polarization storage in ice. This technique was first introduced many years ago by B. Gross¹⁸ for the nonisothermal

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studies of electrets that are now classical. Subsequently, it has also been applied for the investigation of ionic crystals (ionic thermal currents),¹⁹ polymers²⁰ (thermally stimulated depolarization TSD), and with biopolymers and other biological materials²¹ showing the electret effect.

The possible existence of ferroelectricity in hexagonal and cubic ice has been reported in the literature.²² Since the first papers the question was raised (Mascarenhas²³) whether the use of TSC for the inference of the ferroelectric transition might not confuse it with a possible electret behavior arising from relaxation effects or transport properties of the stored polarization. Onsager²⁴ also discussed the question of possible ferroelectricity as reported by Riehl and collaborators with a different interpretation, involving transport mechanisms in ice. Recently, Johari *et al.*,²⁵ using the TSC technique in normal and deuterated ice at different pressures, came to the conclusion that the reported ferroelectricity of ice could indeed be interpreted as a relaxation effect and not as a collective order-disorder transition like the ferroelectric. Johari also pointed out the possible use of the TSC technique with previous polarization with an external electric field, as is normally done in electret work, for the investigation of phase transitions in solids.

In this paper we show that electrical currents can be observed during growth of amorphous ice from the vapor phase, and also during subsequent warming of the condensate. The condensation current is associated with the vapor to solid transition, similar to the Costa Ribeiro Effect¹⁰ for the liquid to solid transition. We present a model for the condensation current that is substantially different from that of Kutzner,²⁶ who carried out the first experiments on this type of current. The second effect, current during heating, is reported here for the first time and it is in essence a TSC spectrum of a natural electret formed by condensation. Current peaks in the TSC spectrum are shown to be of two types: depolarization currents related to dipolar relaxation processes in the condensate and peaks due to phase transitions. The latter occur at the known temperature ranges for the amorphous to cubic and cubic to hexagonal transformations. We have also demonstrated experimentally that these are two general effects occurring not only with water but with many other substances that form amorphous phases during condensation at low temperatures.²⁷

EXPERIMENTAL

Distilled H₂O or D₂O was used for the experiments. Vapor was introduced into an evacuated metal cryostat (Fig. 1) by connecting it to a container filled with liquid. The vapor condensed on a grounded copper electrode M which has been cooled with liquid nitrogen introduced through the cold finger CF. Upon condensation the cryostat could be evacuated continuously via V. Thermocouples continuously monitored the temperature of M. Optical measurements or direct visual observation could be made through window W. For the electrical measurements a Keithley 602 electrometer

was connected between an insulated electrode (IE) and electrode M. The end of electrode IE was suspended over M, and did not touch the ice film. A heater warmed the condensate on M at a rate varying from a few degrees per minute to 80 °C/min and the temperature was simultaneously recorded on a double pen or XY recorder along with the current. A typical experiment was run in the following sequence: After evacuation of the cryostat to about 10⁻³ mmHg, liquid nitrogen (LN) was introduced in the cold finger CF. Water vapor was then introduced and the condensate would form. During the growth of the condensate the current was recorded. After completion of the process the heater was introduced in CF and the warming of the sample and the corresponding TSC spectrum could be observed. Optical observation of the condensate film during warmup clearly showed transition points by changes in light scattered from the sample. Occasionally, the voltage, rather than current, was measured during condensation and warming, but this was not a very sensitive technique and was complicated by drift of the electrometer. The results, nevertheless, were in agreement with the others, i.e., the rate of change of the voltage was proportional, within experimental error, to the currents reported below.

RESULTS

We observed two electrical effects. The first was the appearance of a displacement current as the ice deposit forms on the cold surface M. Figure 2 shows sequential bursts of this current, each one corresponding to a brief introduction of water vapor into the system. The current is the same for growth on the metal or on previously grown layers of amorphous ice. The same occurs for growth on copper, stainless steel, glass, and Teflon. We have not quantitatively measured the instantaneous rate of condensation so we cannot compare this rate with the instantaneous current as done by Kutzner²⁶ and by Pinatti and Mascarenhas during the formation of hexagonal ice.¹³ Nevertheless, we have observed that the condensation current for a given isothermal experiment monotonically decreases as one uses higher and higher condensation temperatures. This is observed from 78 to 150 K. The second type of electrical effect is the appearance of ther-

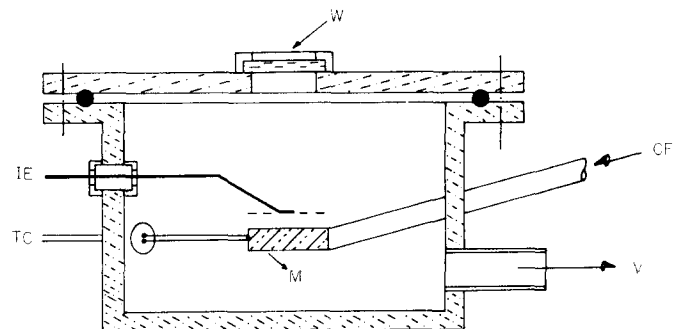


FIG. 1. Experiments apparatus. For most experiments the end of the insulated electrode IE was a point held 0.5 cm away from the grounded electrode M (~2 cm² area). Grids and plates were also used with substantially the same results.

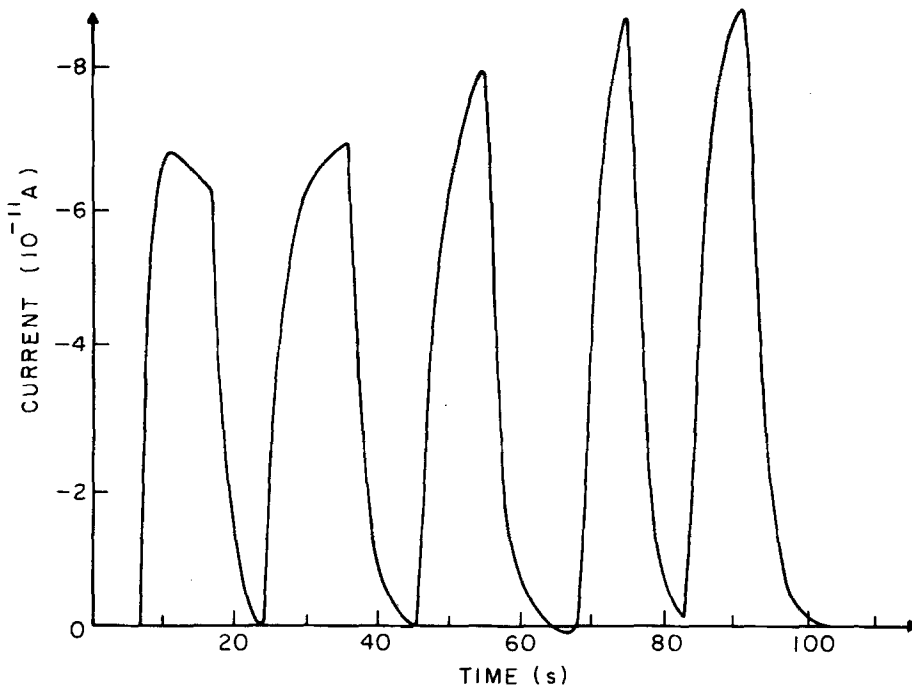


FIG. 2. Current bursts observed during periodic steps of condensation of H_2O at 78°K . The currents are all negative.

mally stimulated currents (TSC) during the warming up of the solid condensate. A typical TSC spectrum is shown in Fig. 3. It consists of broad peaks at ~ 103 , and ~ 130 K, a sharp negative peak at ~ 153 K, and other features at higher temperatures. We carried out experiments to insure that both of these effects were not due to localized charges in the vapor as reported for CO_2 by Mascarenhas *et al.*²⁸ An electrostatic filter was used to trap any existing ions in the vapors, with no appreciable effect on our results. Similarly, an external electric field applied to electrodes IE and M had no influence neither during condensation nor warming.

The following were consistently observed for these effects: (a) The polarity of the condensation current was always negative, i. e., the insulated electrode IE was negative with respect to the grounded electrode M. This was independent of the condensation temperature and nature of grounded electrode. (b) The polarity of the TSC was always opposite to the condensation current except for the sharp peak at ~ 153 K. (c) The integrated charge for both the condensation current and TSC were equal within 10% (experimental error for this type of experiment), indicating charge conservation, i. e., the TSC depolarizes a natural electret formed during condensation. (d) More than 90% of the depolarization of films grown at LNT occurs in the first two peaks of the TSC spectrum.

We now describe a series of cleaning experiments to investigate the relation between the different peaks. The sample is first grown by condensation, and the freezing current is observed. The TSC is then partially measured by warming up the solid sample through the first peak (~ 103 K). The condensate is then cooled back to LNT and a new spectrum is recorded during warmup. This time the ~ 103 K peak is seen to be absent or "cleaned out" of the TSC spectrum but the fol-

lowing peak is recorded. This was repeated for all the main peaks with the result of Fig. 4. It is seen that (i) all of the TSC peaks are irreversible and (ii) that they are completely independent, i. e., the depolarization processes that produce the various TSC peaks are unrelated. We found the same results from experiments on films condensated at different temperatures.

Studies were also made with different heating rates; the shape of the TSC spectrum was not strongly affected, only its magnitude. Faster heating produced higher currents. From Fig. 5(a) one can see that this

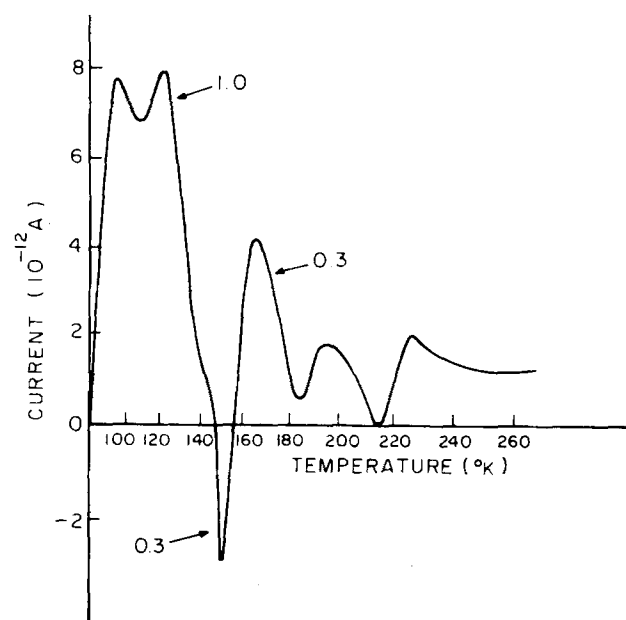


FIG. 3. Current observed during heating of another sample. The upper scale is positive. Note the change in scale multiplier.

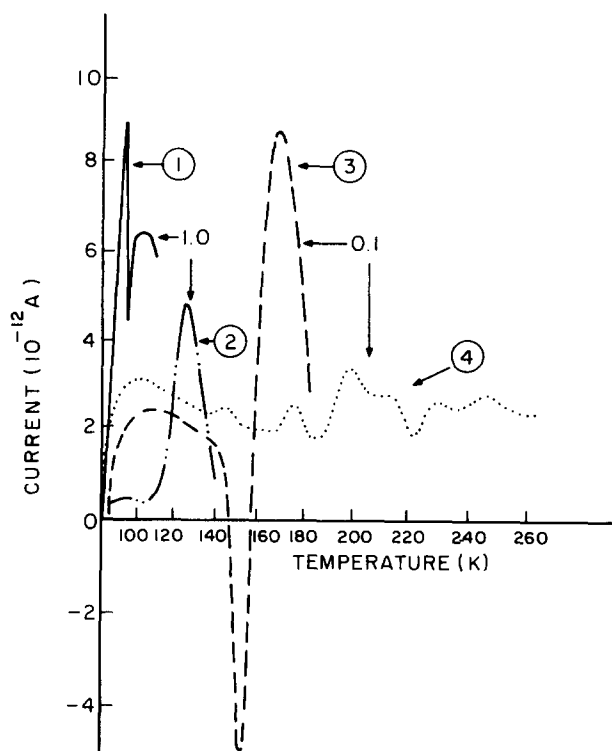


FIG. 4. Cleaning experiments done on one sample by sequential warmings to $\sim 110^\circ\text{K}$ (1), $\sim 140^\circ\text{K}$ (2), $\sim 190^\circ\text{K}$ (3), and $\sim 273^\circ\text{K}$ (4). Note scale multipliers.

increase is approximately linear with heating rate for the narrow peak at $\sim 154\text{ K}$.

Experiments carried out with D_2O produced essentially the same results as for H_2O in all respects. The main difference was a shift of the peaks to higher temperature. For the narrow peak at $\sim 154\text{ K}$ this shift could be easily measured. It was on the order of 4 to 5 K [Fig. 5(b)]. The peaks at lower temperatures appeared to have a slightly higher shift (10 to 15 K) but it was difficult to make quantitative comparisons because these peaks are quite broad.

In some experiments the water was collected on filter paper during heating and by weighing it we could then calculate the mass and thickness of the condensed sample. We found a linear relation between the charge induced on the measuring electrode (IE) and the sample thickness.

DISCUSSION AND MODELS

The main experimental results reported above on the condensation current indicate that it is related to the condensation process itself and is not associated with the trapping of charged ions or impurities. Additionally, in agreement with Kutzner,²⁶ we see no effect of an external electric field, which implies that the current must be due to a reproducible intrinsic process that preferentially aligns the molecular dipoles upon condensation. This would produce a charging current for the following reason: Any preferential orientation of the molecules which condense on the surface will be largely retained as these molecules get buried by the deposition of successive layers. The resulting electric

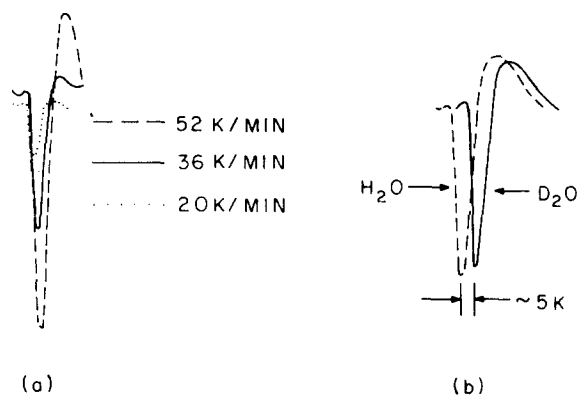


FIG. 5. Effect of (a) heating rate and (b) D_2O on the negative peak.

polarization is equivalent to a net surface charge. Figure 6 shows that as the film grows, the surface charge moves away from one contact (M) and toward the other (IE), inducing the external current through the electrometer (E). After growth, the film has a uniform bulk polarization due to aligned dipoles. Thermally induced reorientation of these dipoles, at various activation energies, gives rise to the TSC spectrum. (An important exception, the sharp peak at $\sim 153\text{ K}$, is discussed later in this paper.) Thus, we are led to the general picture that the condensation current is due to a surface effect and the TSC is a bulk effect, both associated with the growth of polarized ice films.

Our measurements on the induced charge vs sample thickness were used to calculate the value of the surface charge from

$$\sigma_i = -\sigma(x/\epsilon d),$$

where σ_i is the charge induced on the measuring contact, σ is the equivalent surface charge on the film, x is the film thickness, ϵ is the dielectric constant of ice, and d is the distance from the measuring electrode to the metal plate upon which the condensation occurred

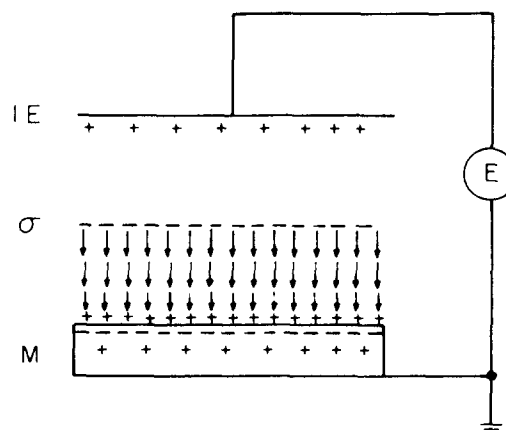


FIG. 6. Pictorial representation of equivalent surface charge (σ) and uniform volume polarization in the film. The arrows represent the molecular dipoles. Also shown are induced charges on grounded cold electrode (M) and measuring insulated electrode (IE) connected to electrometer (E). Motion of the surface charge towards IE induces the negative condensation current.

($x \ll d$). We found that the surface charge density was at least 3.5×10^{-9} coulomb/cm² at 78 K. This means that more than one in 10^5 molecules contribute to the net polarization.

We now justify the underlying reasons for a preferred dipole orientation. It involves the asymmetric distribution of electric field lines about a water molecule; the fields are stronger around the protons. Since a dielectric medium lowers the net energy in an electric field, the proton side of a molecule is preferentially attracted to the substrate during condensation. Thus, the electric dipole of the bound molecule tends to point toward the substrate. If the temperature of the substrate is low enough, dipolar rotation will not occur and the resulting negative surface charge will be frozen in. The next layer of molecules will deposit in the same way and thereby a bulk uniform polarization will build up during growth. This film, and its negative surface charge, are shown in Fig. 6.

In view of the fact that two peaks are seen in the TSC in the amorphous ice temperature range, it is natural to assume that dipoles are trapped in two different configurations corresponding to different energy barriers for reorientation. Using the cleaning technique we were able to separate the higher temperature peak in the amorphous region (at 130 K) from the lower one at 103 K. If dipolar rotation is the relaxation mechanism for depolarization, this current peak should obey monomolecular kinetics and thereby the activation energy for rotation can be obtained from an initial rise analysis, i. e., plotting $\ln I$ vs $1/T$ using the higher temperature shoulder of the cleaned peak. Using this method we have obtained a value of ~ 0.15 to 0.2 eV for the activation energy. The observed temperature shifts for D₂O for the lower temperature peaks is also on the same order of magnitude (10 to 15 K) as those found by Johari (13 K) for hexagonal D₂O ice polarized with an external field.²⁵

The population of oriented dipoles in an as-grown film is expected to depend on condensation temperature. With increasing temperatures, relaxation processes during condensation induce reorientations that tend to decrease the frozen in net polarization. In fact, we have observed a large decrease of both condensation and depolarization currents for increasing deposition temperatures. This is also in agreement with our results that the various depolarization peaks of the TSC spectrum are completely independent. Also, we have observed that only a small fraction of the polarization is frozen in (10%) for condensation temperatures above 130 °C, where relaxation reorientation has already taken place, as indicated by the depolarization at 103 and 130 K.

We now discuss the existence of the sharp negative peak at 153 K. This peak occurs exactly at the temperature range of the amorphous to cubic transition determined by independent methods such as differential thermal analysis²⁹ and reflectivity changes³⁰ done at heating rates similar to those used here. Furthermore, our D₂O experiments show a 5 K peak shift in agreement with

that found by the use of electron diffraction.³¹ We have also made optical observations simultaneously with our TSC experiments confirming the onset of a phase transition at the temperature where the 153 K peak occurred. We propose that the growing cubic phase will tend to polarize itself with the same polarity of the remaining amorphous ice. In this way the phase charge could increase the net polarization of the sample.

In some of our experiments we have observed a similar negative current peak at the temperature range of the cubic to hexagonal transition. This was weak and broad as one would expect since this transition is known to occur at much slower rates.³⁰

CONCLUSIONS

During formation of ice from the vapor phase on a cold substrate a condensation current is observed. This is probably due to the formation of a natural electret with a net internal polarization. The polarity of the condensation current is consistent with the proton side of the molecule facing the substrate. The asymmetry of the electric field line around the molecule is suggested as the basic cause for the preferred orientation. During heating of the condensate current, peaks of two types are seen: (i) those due to reorientation of H₂O dipoles in the bulk of the condensate, producing current peaks with opposite polarity to the condensation current; and (ii) those due to phase transitions. The polarity of the phase transition peaks is the same as that of the condensation current, consistent with an increase of the sample polarization during growth of the new phase. D₂O shifts both types of peaks in good agreement with observations of other authors using different techniques.

The observed effects may be important as new techniques for the investigations of surface phenomena and phase changes in the solid state using the simple concept of preferred orientation during the condensation of asymmetric dipolar molecules.

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