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Sublimation of vapor-deposited water ice below 170 K, and its dependence on growth conditions

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The sublimation of vapor-deposited H_2O ice films was investigated between 60 and 170 K using a piezoelectric microbalance and a mass spectrometer. The films were grown in vacuum at substrate temperatures between 30 and 120 K and rates between 0.2 and 7 μm/h. Above 140 K, the sublimation rate did not depend on the growth conditions tested and yielded a sublimation energy of 0.45 ± 0.03 eV. Below 140 K, we found that fresh films have an enhanced sublimation rate, which decays in time and which depends on film thickness and growth temperatures. This is attributed to sublimation from regions containing amorphous ice, which transforms with time into the less volatile crystalline ice, with an activation energy of 0.44 ± 0.04 eV. The finding of a dependence of sublimation and crystallization rates on growth conditions can explain large discrepancies in the data published during the last four decades.

I. INTRODUCTION

In spite of the importance of vapor-deposited water ice both in our solar system and interstellar space, its properties are not well known. Although the common phases have been well studied, large gaps still exist in our knowledge of the phases formed from vapor deposition at the very low temperatures and pressures of many astronomical environments and laboratory cryogenic systems.[1-3] The phases identified below 170 K are cubic crystalline ice, I_c, and different types of amorphous ice, I_a.[4-7] How the phases form depends on growth conditions, such as temperature and growth rate.[5,8-10] For instance, films condensed below 130 K at growth rates less than 100 μm/h are reported to be amorphous.[4,5,8,11] The finding that low condensation rates at $T<77$ K produce I_a and that higher rates produce I_c,[8,12] also seen in other molecular solids,[13,14] is surprising since it is against expectation based on studies of other solids.[15] To grow amorphous films of other materials, one needs high condensation rates to prevent significant diffusion of the molecules to more stable crystalline sites. The amorphous phase of ice is metastable and transforms into crystalline ice; a long-standing puzzle has been that different studies have found contradictory results for the rate of crystallization, differing by orders of magnitude at a given temperature.[16-20]

The physical properties of ice, such as density or thermal properties, depend strongly on its structure.[4,21,22] One such quantity is the sublimation rate, which is very important in determining the evolution of surfaces of samples for cryomicroscopy[3] and surfaces of astronomical objects in low-temperature environments such as comets,[23,24] Saturnian ring particles,[25] the icy satellites in the outer solar system,[26] and icy interstellar grains.[27]

Recently, Kouchi reported that the vapor pressure of ice depends strongly on growth temperature and rate.[11] He found that the vapor pressure of I_a condensed slowly at low temperatures is up to two orders of magnitude higher at around 130 K than that of I_c. These results, obtained with mass spectrometry, differed from earlier sublimation-rate data obtained by Bryson, Cazcarra, and Levenson with a microbalance,[28] which are correlated through the vaporization coefficient to the vapor pressure,[29] and with observations by Dubochet *et al.* in a cryoelectron microscope.[30] In a later paper, Kouchi presented a second set of measurements on ice films again grown at low temperatures and low growth rates.[14] Although these results did not agree with their previous data,[11] they also show that I_a has a much higher vapor pressure below 130 K than I_c. Similar conclusions can be derived from the relative sublimation rates of Livesey *et al.*[31] More recently, Bar-Nun, Notesco, and Laufer[32] could not reproduce Kouchi's results, but found that the vapor pressure of amorphous ice is at most 3 times higher than that of crystalline ice.

To clarify the reasons for these contradictory results, we undertook studies of sublimation of ice films grown from the vapor phase under a variety of conditions. Since we suspected that previous findings may be affected by the condensation of impurities from the residual vacuum in the system, we took special care in growing pure ice films under ultrahigh-vacuum conditions. Sublimation rates were derived from mass losses measured with a

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very sensitive microbalance. The results suggest causes for previous disagreements between different researchers and provide a new insight on the dependence of the properties of ice on growth conditions.

II. EXPERIMENTAL DETAILS

Ice films were grown in an ultrahigh-vacuum chamber (base pressure $10^{-11}-10^{-10}$ Torr) at substrate temperatures between 30 and 120 K and growth rates between 200 and 7000 nm/h. The films were produced by diffusing water vapor through a capillary array doser[33] onto a cooled, gold-coated quartz crystal microbalance at normal incidence (Fig. 1). The capillary array has a diameter of 25 mm, a thickness of 0.5 mm, and holes with a diameter of 50 μm, each approximately 120 μm apart. The sample is cooled by a closed-cycle refrigerator and heated to the desired temperature at a rate of about 1 K/min. Two cooled metal cans, surrounding the substrate, shield the ice film from heat radiation from room-temperature surfaces; the inner can, which is kept at 12 K, also serves as an additional cryopump to keep a clean environment in the vicinity of the sample. This improved the ratio of water vs impurity deposition during film growth to more than 10^4. The holes in the cans, used for gas dosing, faced a cold plate during the measurements to prevent the sample from being exposed to thermal radiation from room-temperature surfaces.

In the quartz-crystal microbalance technique, changes in the areal mass of thin deposits cause a change in the resonance frequency of the quartz crystal, driven at its natural frequency. Since the frequency also changes with temperature, we use a heterodyne method with another crystal mounted on the back side of the target which was not exposed to gases. The sublimation rate (or flux) is then derived from the rate of change of the frequency difference between the two crystals, with a very small residual temperature effect that limits the sensitivity to the equivalent of $\sim 5\times 10^{11}$ H_2O mol/cm^2/s or about 0.0005 monolayer/s. In the temperature range investigated, this corresponds to a vapor pressure of about 5×10^{-10} Torr, assuming the vaporization coefficient to be unity.[28] Typical measurement times at one temperature were of the order of 15 min.

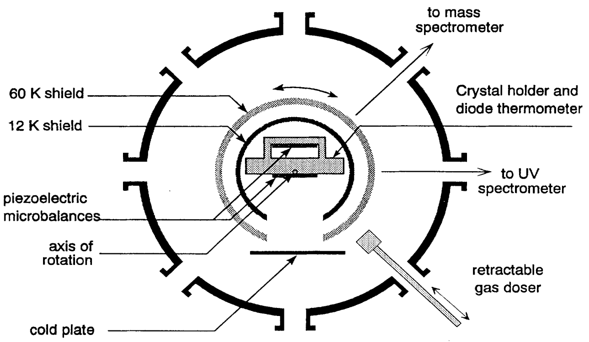

FIG. 1. Experimental setup. The sample can be rotated together with the cans to face any port or the cold plate to prevent significant thermal radiation from reaching the ice.

The water used for the experiments was HPLC-grade H_2O; it was thoroughly degassed before use. The purity of the water was checked by analyzing the material subliming from the target between 60 and 180 K with a mass spectrometer. Only small traces of CO were found; the total impurity content in the film was below 0.5%.

III. RESULTS

A. Sublimation rates between 135 and 170 K

Figure 2 shows the sublimation rate (or flux) $\Phi(T)$ of 1.2-μm-thick water ice films in the 130–170-K temperature range. We varied the growth temperature and growth rate over a broad range and, in one experiment, also the film thickness. It can be seen that above 140 K Φ does not depend strongly on the growth conditions in the investigated temperature range. The scatter of the data at 135 and 140 K will be discussed later. To verify previous reports[14] we attempted to measure $\Phi(T)$ between 60 and 130 K for ice films grown under various conditions, but found in all cases that it was lower than our sensitivity limit.

The vapor pressure of polyatomic molecules can be written in the form[6,34]

$$p_v = cT^4 \exp(-E_{\text{sub}}/kT) \, , \tag{1}$$

where T is the surface temperature, E_{sub} the sublimation energy, and c a constant. From gas kinetic theory, the relation between the vapor pressure p_v and the sublimation rate is

$$p_v = c' T^{0.5} \Phi(T) \, . \tag{2}$$

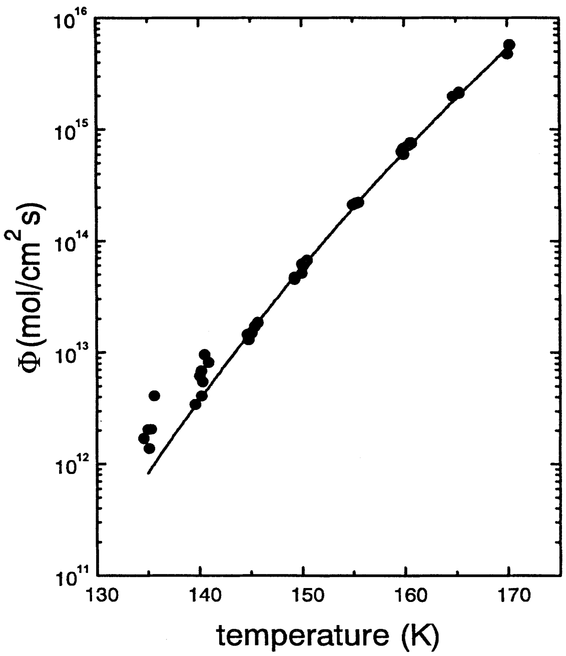

FIG. 2. Sublimation rate of 1.2-μm-thick water ice films as a function of temperature; the films were grown at different temperatures and growth rates. See text for scatter of the data for $T \leq 140$ K and the fit shown by the solid line.

Therefore we fit our data using the expression

$$\Phi(T)=c''f_a T^{3.5}\exp(-E_{\mathrm{sub}}/kT) . \quad (3)$$

The areal factor f_a, equal to the ratio of effective surface area to geometric area, takes into account the possibility that sublimation from a rough surface could be higher than that from a plane surface. From the fit in Fig. 2, the heat of sublimation, E_{sub}, is 0.45±0.03 eV and $c''f_a=1.82\times10^{21}$ mol/(cm^2 s K$^{3.5}$). This value is in good agreement with that for annealed ice obtained by Sandford and Allamandola by measuring sticking coefficients:[35] They also derived a heat of sublimation of 0.44 eV for annealed ice and 0.41 eV for as-deposited ice. Other published values for polycrystalline ice are 0.49 eV from Bryson, Cazcarra, and Levenson[28] and 0.51±0.1 eV from Haynes, Tro, and George;[36] both were obtained without considering the factor T^4 [Eq. (1)] in the expression for the vapor pressure. Including this factor, these values would be the same as ours within errors.

In addition to the mass-loss measurements, we observed sublimation with a quadrupole mass spectrometer in line with the target.[37] The sublimation energy derived from the variation of the partial pressure of H_2O with temperature is the same, within errors, as that measured with the more accurate microbalance.

B. Sublimation rates (measured near 135 K) for films deposited and grown at lower temperatures

At first we thought that the scatter of the data at low temperatures was due to statistical fluctuations due to the small amount of material removed. However, additional experiments showed systematic deviations of the data at around 135 K. First, we grew a 1.5-μm film at 60 K and measured Φ(135 K). Then, we heated the film to 155 K; after about 10 min, the sample is expected to have converted completely to crystalline ice.[16–20] The film was then cooled back down to 135 K and Φ was found to be lower by a factor of 3, and the value agreed with the fit to Eq. (3). In another experiment, we grew a film at 60 K, heated it up to 135 K, and then measured Φ as a function of time. Φ dropped with time and approached a constant value Φ^{ann}, which is in agreement with the solid line in Fig. 2.

We investigated this drop of Φ in time in more detail at 135 K for various film thicknesses, growth temperatures, and growth rates. In the following we describe the ice films as follows.

(1) "Fresh." These films were grown at a temperature $T_g<120$ K and then warmed up to 135 K. These films are, presumably, initially amorphous,[4,5,22] although they can contain polycrystalline grains embedded in the amorphous phase even when grown below 100 K.[38] These films are metastable and transform into crystalline ice at a rate that depends on temperature.

(2) "Annealed." These films were heated up to 155 K for 10 min, conditions which are known to lead to cubic crystalline ice.[16–20] During this time, the films also lose about 30 monolayers of H_2O. After this, we lowered the temperature to 135 K and measured the sublimation rate Φ^{ann} and found it to be 5.7×10^{11} mol/cm^2/s, in agreement with Eq. (3). We found this value to be independent of film thickness, growth temperature, and growth rate within errors of 10%.

Since films grown at any T_g eventually transform to the stable crystalline phase, reaching Φ^{ann}, we use $\Delta\Phi=\Phi-\Phi^{\mathrm{ann}}$ as a measure of the deviation from this annealed condition. Figure 3(a) depicts $\Delta\Phi$ for ice films of various thicknesses, grown at 60 K at a rate of ~230 nm/h. The origin of time is when the film reaches 135 K, after being warmed up at 1 K/min. It can be seen that the excess sublimation rate drops roughly exponentially with time as

$$\Delta\Phi=\Delta\Phi^0\exp(-t/\tau) . \quad (4)$$

We find that while τ is independent of thickness, the "initial" excess sublimation rate $\Delta\Phi^0$ increases with increasing thickness, as shown in Fig. 3(b). Experiments with 1.2-μm films grown at 60 K showed no dependence of $\Delta\Phi^0$ or τ on the *growth rate* in the range from 230 nm/h to 38 μm/h, within the experimental uncertainty of ±15% in $\Delta\Phi^0$ and ±10% in τ. On the other hand, varia-

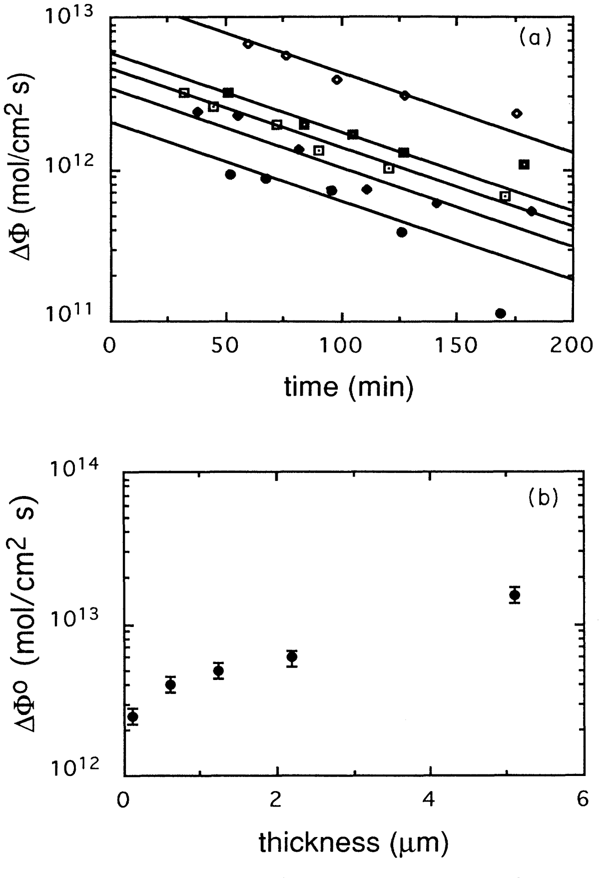

FIG. 3. (a) Excess sublimation rate $\Delta\Phi$ at 135 K of H_2O films grown at 60 K (growth rate 230 nm/h) as a function of time after reaching 135 K. Film thickness is μm: 0.12 (●), 0.61 (♦), 1.2 (□), 2.2 (■), and 5.1 (◇). For curve fits; see text. (b) Initial excess sublimation rate $\Delta\Phi^0$ of films shown in (a), as a function of film thickness. The error bars represent the uncertainty in the fits to (a).

tion of the *growth temperature* T_g for 1.2-μm films grown at 230 nm/h affected both τ and $\Delta\Phi^0$.

A quantity of interest is the total additional amount of ice that sublimes due to the excess sublimation rate before Φ^{ann} is reached. This quantity, $\Delta\Phi^0\tau$, is obtained by integrating $\Delta\Phi$ over time and is depicted in Fig. 4(a) as a function of $1/T_g$. The dependences of $\Delta\Phi^0$ and τ on $1/T_g$ are shown in Figs. 4(b) and 4(c). The initial sublimation rate $\Delta\Phi^0$ shows a maximum at around 85 K. The data in Fig. 4(c) can be fit by the equation

$$\tau = 1.35\times10^3 \text{ s} \exp(5.4 \text{ meV}/kT_g) . \quad (5)$$

In addition, we varied the sublimation temperature T_{sub} between 132 and 138 K for a 1.2-μm film grown at 60 K. We found

$$\tau = 1.13\times10^{-13} \text{ s} \exp(0.44 \text{ eV}/kT_{\text{sub}}) , \quad (6)$$

whereas $\Delta\Phi^0\tau$ was found to be independent of T_{sub} between 132 and 138 K within the experimental uncertainty of ±15%.

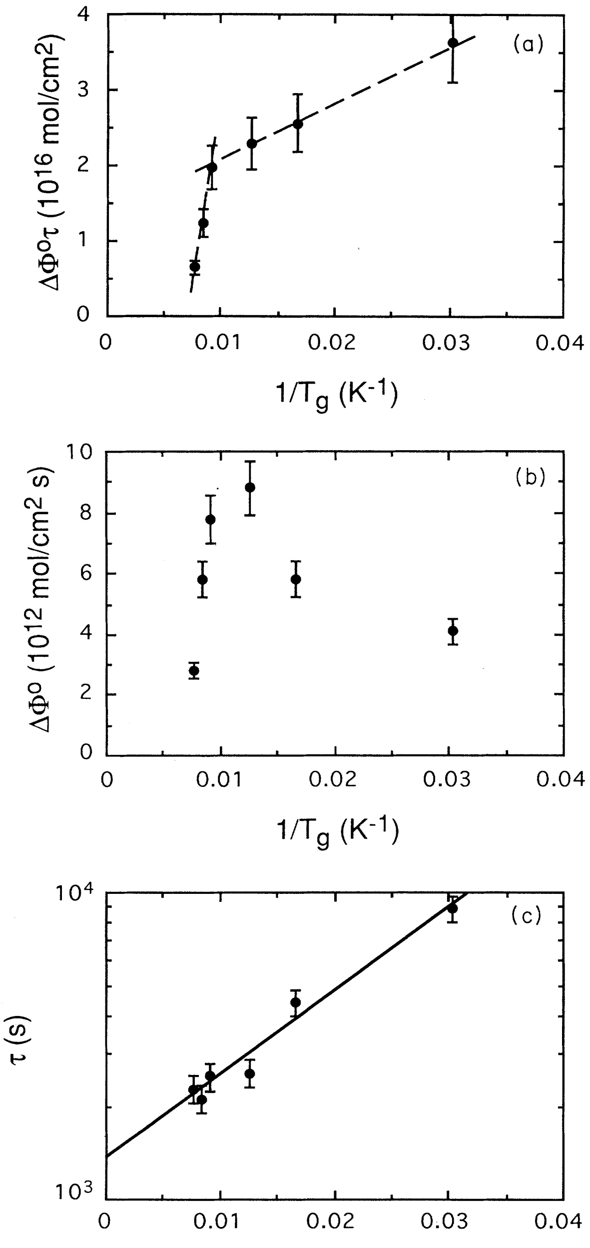

FIG. 4. Sublimation data at 135 K of water ice for various growth temperatures T_g (1.2 μm, growth rate 230 nm/h): (a) total amount of ice removed before sublimation rate reaches Φ^{ann}; (b) initial sublimation rate of fresh films; (c) time constant for phase transformation at 135 K; for curve fit, see text.

In summary, the following are the main results of this work.

(1) The sublimation rate between 140 and 170 K of fresh-water ice films vapor deposited below 120 K does not differ significantly from that of ice films annealed at 155 K for 10 min. The sublimation energy is 0.45±0.03 eV.

(2) Fresh vapor-deposited films show a high initial sublimation rate at 135 K, which drops exponentially with time and approaches a constant value equal to that of annealed ice. The initial sublimation rate depends on the thickness of the film and the growth temperature but not on the growth rate. The growth temperature is also found to influence the time constant of the decrease of the sublimation rate. The total additional material removed during the transformation $\Delta\Phi^0\tau$ increases with decreasing growth temperature and with increasing film thickness, but is independent of the sublimation temperature.

IV. DISCUSSION

Our results confirm the observations of Kouchi[11,14] of a higher sublimation rate for fresh films condensed at low temperatures. Our finding of a decay of the sublimation rate with time can be understood by assuming that the fresh films contain amorphous ice which is more volatile than crystalline ice ($\Phi^a > \Phi^c$);[11,35] the time evolution of the sublimation rates is then connected with the transformation of the amorphous ice into the less volatile crystalline ice, according to

$$c_a = c_a^0 \exp(-t/\tau) , \quad (7)$$

where c_a is the concentration of amorphous ice and c_a^0 its initial value. Then

$$\Phi(t) = \Phi^a c_a + \Phi^c(1-c_a) \quad (8)$$

and

$$\Phi(t) - \Phi^c = (\Phi^a - \Phi^c) c_a^0 \exp(-t/\tau) , \quad (9)$$

which is equal to Eq. (4) if we set $\Phi^c = \Phi^{\text{ann}}$.

Our results can then be interpreted from Eq. (9) by assuming that thin fresh films, although grown at 60 K, are not purely amorphous but contain some crystalline grains and that the initial amorphous content c_a^0 increases with film thickness. This could be due to polycrystalline growth of water ice on the gold substrate. The fact that even for the lowest thickness of 0.12 μm there is still an initial excess sublimation suggests that even the thinnest films are not completely crystalline. The thicker the film, the less influence the substrate has on the structure of the ice and the more amorphous is the film, yielding an increase of $\Delta\Phi^0$ with increasing thickness. From Fig. 3(b) we can derive a maximum $\Delta\Phi^0$ in the thickness range studied of about 1.5×10^{13} mol/cm^2/s.

Under the assumption that the time decay of Φ reflects the irreversible phase transformation to I_c, we can derive an activation energy for crystallization from the dependence of τ on the sublimation temperature [Eq. (6)]. We obtain 0.44 ± 0.04 eV for a 1.2-μm film grown at 60 K, in good agreement with the value of 0.46 eV obtained by Schmitt, Grim, and Greenberg by analyzing crystallization using infrared-absorption data.[20] The range of τ obtained at 135 K, shown in Fig. 4(c), includes the value of 3×10^3 s derived from Dowell and Rinfret[17,39] and is roughly consistent with 1.8×10^4 s obtained by Schmitt, Grim, and Greenberg[20,40] for films grown at 10 K.

The observation that $\Delta\Phi^0\tau$ was independent of the sublimation temperature between 132 and 138 K can be understood by noticing the similar values of the sublimation energy and activation energy for crystallization: A higher T_{sub} causes higher sublimation rates, but also a higher crystallization rate.

The two regions in Fig. 4(a), indicated by the dashed lines, might be related to the formation of two different forms of amorphous ice which have been proposed to exist.[41] The peak at 85 K, seen in Fig. 4(b), coincides with the threshold temperature above and below which different amorphous forms result upon condensation.[41]

Enhanced sublimation rates could possibly also be caused by a high surface roughness. It has been previously reported that the surface of vapor-deposited water ice grown below 150 K is very irregular. Laufer, Kochavi, and Bar-Nun[41] observed the growth of needlelike structures in pure and gas-filled amorphous ice condensed below 100 K. Mayer and Pletzer[9] identified tiny "stalactites" formed when using a gas doser under conditions believed to lead to clustering of water molecules. Ghormley[21,42] and Mayer and Pletzer[10] found that fresh amorphous ice grown at 20 K has a very large surface area, which they attributed to a large micropure volume and which decreases when heated to 77 K. We expect that molecules in less strongly bound sites (as, e.g., on edges and tips of needles on the surface) are easier to remove during the sublimation at 135 K than others. Then the film may become less rough with time and hence Φ could decrease.

A rough surface could even by itself lead to higher sublimation rates, since the real surface area of a fresh film might be higher than the geometrical one, making f_a [Eq. (3)] larger than 1. A reduction in surface area accompanying the smoothing process might explain the decrease in Φ. However, it seems improbable that increasing surface roughness with increasing film thickness alone could lead (as in the case of the 5.1-μm film) to sublimation rates 30 times higher than those of annealed films. Molecules subliming from a rough surface which hit the ice surface again will most likely recondense and not contribute to Φ, since sticking coefficients are high at 135 K. We therefore favor the explanation of a phase transformation at 135 K for the time dependence of Φ.

Our results suggest an explanation for Kouchi's observation of a peak at 130–140 K in the dependence of vapor pressure with temperature.[11] The fresh films analyzed there are initially mostly amorphous, leading to higher sublimation rates than those of crystalline films. The vapor pressure is measured as the samples are warmed up at a steady heating rate of 1 K/min; e.g., they were not obtained in equilibrium. As a result of the variation of T with time, there is a competition between the increase of Φ due to the increase in temperature and the decrease of Φ as the more volatile amorphous ice transforms into crystalline ice. This causes a maximum in the Φ vs T curve which, we propose, would not appear at much lower heating rates. This is shown in Fig. 5 where we modeled the sublimation rate as a function of temperature for films heated at different rates using our data for τ and assuming $E_{\text{sub}}=0.4$ eV for I_a.

The peak around 135 K in Kouchi's data has the largest height and width for a film grown at $T_g=85.2$ K, smaller heights for higher temperatures and a smaller width for $T_g=75.4$ K. This is consistent with our findings that the highest initial sublimation rate $\Delta\Phi^0$ is obtained for films grown at around 85 K [Fig. 4(b)]. The data by Bar-Nun, Notesco, and Laufer also show the highest sublimation rates for films grown at 75 K.[32] Our results differ from Kouchi's later data where the vapor pressure of H_2O ice grown at 10 K at the rate of 80 nm/h was found to be above 2×10^{-9} Torr between 85 and 130 K with a maximum at 90 K.[14] Our measurements gave

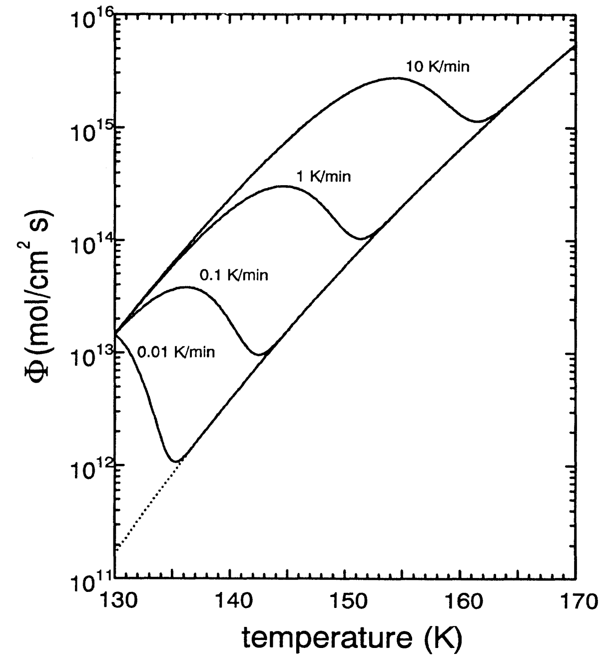

FIG. 5. Calculated sublimation rate vs temperature for an initially amorphous film heated at different rates. The time constant for crystallization is that for a film grown at 60 K [Eq. (6) in text]. The dashed line is the sublimation rate of crystalline ice.

values lower than our sensitivity limit of the vapor pressure of $\sim 10^{-9}$ Torr in this temperature range. At the higher end of our temperature range, our data are in good agreement with the results by Bryson, Cazcarra, and Levenson for crystalline ice.[28]

The dependence of amorphous content with growth temperature T_g suggested by Fig. 4(a) can be used to explain that of the crystallization rate in Fig. 4(c), since it is reasonable to expect a faster crystallization the larger the content of I_c. This is a simplified explanation, since τ should depend also on the size distribution of the crystallites. The divergent values of τ given by different workers can be explained by different contents of I_c,[8,43,44] depending on the particular growth conditions including substrate used.

In conclusion, fresh ice films have higher sublimation rates than crystalline ice, indicating a lower sublimation energy. The sublimation rates do not depend only on the temperature of the ice, but also on its history, including the way it was formed. These observations allow reconsideration of previous, apparently conflicting measurements and explain them by difference in the content of crystalline ice in films grown under different conditions.

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