

# Crystallization kinetics of water below 150 K

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Metastable liquid water, obtained by heating its hyperquenched glassy state above its glass→liquid transition temperature, crystallizes to cubic ice. Kinetics of this crystallization has been studied by Fourier transform infrared spectroscopy by determining the change in the spectra of stretching vibrations of the decoupled OD oscillator in 3.6 mole % HOD in H<sub>2</sub>O. The crystallization kinetics follows the equation  $x = [1 - \exp(-kt^n)]$  and is diffusion controlled. Annealing at a temperature below its glass→liquid transition temperature alters this kinetics as the grain-growth process begins to control the early stages of crystallization.

## I. INTRODUCTION

Liquid water in form of  $\mu\text{m}$ -sized droplets can be vitrified on a cryoplate by so-called hyperquenching at cooling rates of  $\approx 10^6$  to  $\approx 10^7 \text{ K s}^{-1}$ .<sup>1-5</sup> This amorphous form of water undergoes a calorimetrically reversible glass→liquid transition with an onset temperature, or  $T_g$ , at 136 K when heated at a rate of  $30 \text{ K min}^{-1}$ .<sup>1,2</sup> On further heating above  $T_g$ , its state is that of a highly viscous liquid which is in internal equilibrium, but metastable with respect to crystallization. Continued heating causes it to crystallize to cubic ice at a rate that increases with temperature.<sup>1-3</sup> In the temperature range 140 K to 150 K, its crystallization rate is slower than that of supercooled water from below 273 K to the temperature of homogeneous nucleation.<sup>6</sup> On further heating above 150 K, its rate of crystallization obviously increases. Thus, there are two ranges of temperature, one above  $T_g$  and the second below  $T_m$ , where metastable water is expected to have similar crystallization rates. But, two different solids, namely cubic and hexagonal ice, are formed by two different kinetics-controlling mechanisms.

Near the glass transition temperature, the metastable liquid's viscosity is high and its crystallization kinetics becomes diffusion controlled. Here, the molecular diffusion time also has a broad distribution, unlike that immediately below  $T_m$  where this distribution is narrow and negligible. Therefore, further differences in the crystallization kinetics of metastable water at  $\approx 150 \text{ K}$  and  $< 273 \text{ K}$  are expected. Isothermal studies of the crystallization kinetics of metastable water have been difficult in both temperature ranges, and, as far as we are aware, have not been done. Here, we describe first study of this kinetics of nucleation and grain growth in highly viscous water obtained by heating its hyperquenched glassy state. It has been determined by Fourier transform infrared (FTIR) spectroscopy in which the evolution of the sharp band for the cubic ice in the decoupled OD stretching region at  $\sim 2420 \text{ cm}^{-1}$  was followed as crystallization of water progressed.

We note that previous crystallization studies below 273 K were done mainly with the intention to differentiate be-

tween homogeneous and heterogeneous nucleation, and to determine the rate of ice crystal growth (reviewed in Ref. 7). We further mention that the crystallization kinetics of vapor-deposited amorphous solid water was investigated by Koverda *et al.*<sup>8</sup> These studies were done by differential thermal analysis in temperature scanning experiments. Because of that, and because of the complexities in the crystallization kinetics of vapor-deposited amorphous solid water,<sup>9</sup> they are not included here in the discussion.

## II. EXPERIMENTAL PROCEDURE

Hyperquenched glassy water was prepared by rapid cooling of an aerosol on a BaF<sub>2</sub> window held at 78 K.<sup>1-5</sup> The aerosol was produced by means of an ultrasonic nebulizer operating at 3 MHz (LKB instruments, Model 108) and transferred with nitrogen as carrier gas through a 400  $\mu\text{m}$  aperture into a high vacuum system containing the low temperature infrared cell. Once inside, the droplets moved towards the BaF<sub>2</sub> window at supersonic speeds and deposited on it. The temperature of the BaF<sub>2</sub> window was measured with a calibrated thermocouple in contact with the copper ring on which the window was mounted. The temperature was regulated with a thermocontroller (AP Paar, Model TTK-HC) and remained constant within  $\pm 0.1$  degree. The temperatures were calibrated by the method described by Ford *et al.*<sup>10</sup> by following the melting of ethylacetate, and was found to be accurate within 0.5°. Measurements were made with D<sub>2</sub>O (2 wt %) in H<sub>2</sub>O, so that the decoupled OD stretching band could be studied. For this HOD concentration, OD-OD interactions do not contribute to the bandwidth of the decoupled OD stretching transition. The OD stretching band is therefore narrow and so any change in it can be accurately and conveniently investigated with progress of crystallization. Hyperquenched glassy water necessarily contains a fraction of the vapor-deposited amorphous form, which depends on density of the aerosol and on its temperature.<sup>5</sup> This fraction was kept constant for each experiment by using close to identical conditions during deposition of the aerosol droplets, and had been estimated previously to be  $< 5\%$

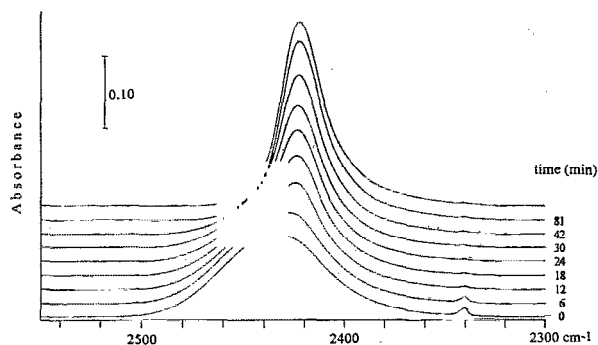


FIG. 1. Typical FTIR spectra in the OD stretching region of HOD in  $\text{H}_2\text{O}$  at 144 K. The spectra are shifted upwards for clarity as indicated. Each spectrum was obtained after keeping the sample for  $t$  s, as indicated, during which part of the water crystallized to cubic ice. As this occurs, the broad peak centered at  $2430\text{ cm}^{-1}$  gradually vanishes and the sharp peak at  $2420\text{ cm}^{-1}$  evolves. The small peak at  $2340\text{ cm}^{-1}$  is due to uncompensated  $\text{CO}_2$ . The ordinate scale refers to all spectra.

for high aerosol density.<sup>4</sup> One of us, E. Mayer, has reported a peak maximum for the decoupled OD oscillator of  $2416\text{ cm}^{-1}$  at 16 K.<sup>5</sup> This value was obtained by cooling the aerosol to  $\approx 273\text{ K}$  and by choosing a high aerosol density. In this study, a lower aerosol density was chosen to minimize the amount of crystalline ice. The OD peak value in this study is  $2424\text{ cm}^{-1}$  for 78 K and  $2430\text{ cm}^{-1}$  at 144 K. It is expected to decrease further at lower temperatures and to approach that reported at 16 K.<sup>5</sup>

The spectra were recorded *in situ*, with base pressure  $\leq 6 \times 10^{-6}$  mbar. This low base pressure is important because under these conditions condensation of water vapor on the cryoplate in form of ice during the experiment is negligible. The FTIR spectra were recorded in transmission on Bio Rad's FTS 45 at  $2\text{ cm}^{-1}$  resolution (UDR 1), by coadding 16 scans for each spectrum. Early during the experiments the spectra were collected at intervals of  $\sim 3$  min. This interval increased thereafter to 10–15 min. The time taken to obtain a spectrum was 90 s. This measurement time is much less than the time of between 1 to 5 h needed for complete crystallization, and was taken into account in determining the crystallization rate.

When the shape of the spectrum at a given temperature showed no change after an interval of 15 min, the sample while still inside the spectrometer was heated to 155 K, kept at 155 K for 20 min, and cooled to the initial temperature and its spectrum remeasured. At 155 K, the sample completely crystallized within 20 min and no sublimation of the sample, which could reduce its thickness, occurred. Thus, complete crystallization of water to cubic ice was ensured. This spectrum therefore corresponded to a completely crystallized state attainable by keeping a sample isothermally for an almost infinite period.

### III. RESULTS

The IR spectra of HOD in  $\text{H}_2\text{O}$  during the course of its crystallization at 144 K are given in Fig. 1. These show that the shape continuously changes with time while crys-

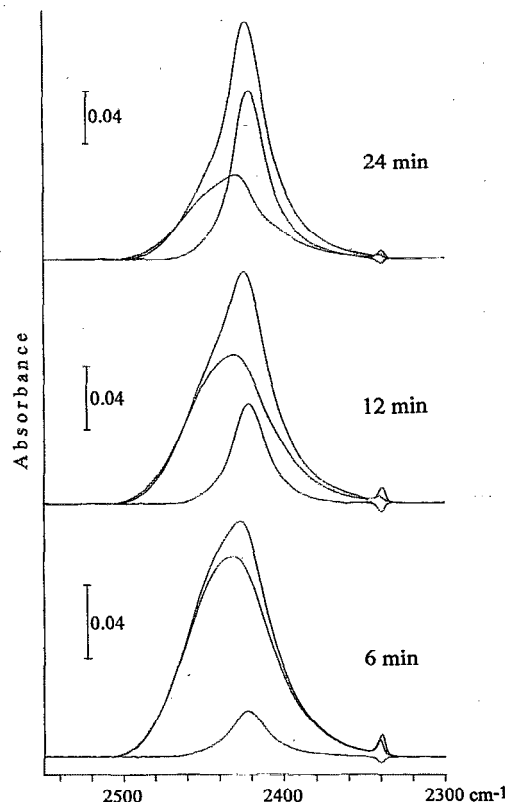


FIG. 2. Resolution of the spectrum for the metastable glassy (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water and cubic ice shown for  $t=0$ ,  $t=6$  min and  $t=24$  min. The base-line corrected original band contours, and the resolved bands for the amorphous and crystalline fractions are shown. Ordinate scales are included.

tallization to cubic ice proceeds. Initially, the spectrum consists of a broad peak centered at  $\sim 2430\text{ cm}^{-1}$  with a small feature near  $2420\text{ cm}^{-1}$ . As water crystallizes, the broad peak at  $2430\text{ cm}^{-1}$  becomes weaker and ultimately vanishes and a sharp peak at  $2420\text{ cm}^{-1}$  evolves. The broad peak is due to the stretching vibration of the uncoupled OD oscillators in water and the sharp peak due to that in cubic ice.

The progress of crystallization was followed by subtracting the spectrum obtained at time zero, from the spectra at time  $t$ , and by determining the intensity of the band attributable to cubic ice. That means that from each spectrum recorded at time  $t$  (which consists of a mixture of the unchanged amorphous water and of the crystallized fraction) the amorphous fraction (represented by the spectrum at time  $t=0$ ) is subtracted and so only the spectrum of the crystallized fraction remains. The subtraction factor is varied until the remaining band of the crystallized fraction is symmetrical and shows the same shape as the band of the spectrum recorded at time  $t \rightarrow \infty$  (i.e., after heating to 155 K and recooling) which corresponds to the completely crystallized state. The resolved bands for the amorphous and crystalline fraction for the spectra obtained after 6 min, 12 min, and 24 min at 144 K are shown in Fig. 2. The resolved band of the amorphous fraction in the spectrum recorded after 24 min shows asymmetry at low frequency

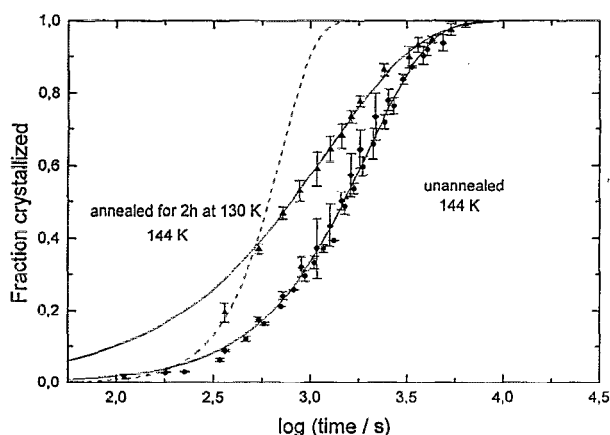


FIG. 3. The fraction of water crystallized at 144 K is plotted against logarithmic time.  $\bullet$  and  $\blacklozenge$  refer to two independently prepared samples, with error bars shown for each value obtained from the spectrum analysis.  $\Delta$  refer to a third independently prepared sample which was annealed for 120 min at 130 K prior to raising its temperature to 144 K. The smooth line shows the calculated values from Eq. (1) with  $k=3.9 \times 10^{-5} \text{ s}^{-n}$  and  $n=1.34$  for the unannealed sample, and with  $k=1.2 \times 10^{-7} \text{ s}^{-n}$  and  $n=2.43$  for the annealed sample. The dashed line was calculated with  $k=1.7 \times 10^{-3} \text{ s}^{-n}$  and  $n=0.90$ , describing the early stage of the crystallization of the annealed sample. The figure shows the reproducibility of the data obtained by two independent measurements and analysed by two independent workers. It also shows the adequacy of Eq. (1) in describing the data and the effect of annealing on the kinetics of crystallization.

which is caused by the subtraction procedure. Asymmetry at high frequency is caused by unavoidable contamination with vapor-deposited amorphous solid water.<sup>5</sup> The subtraction was done independently by two workers, and the mean of the difference between the resolved peak heights of the band due to the crystalline ice was taken as error in our analysis. This error varied from one spectrum to another. It was more at the beginning of each experiment where the amount of cubic ice is small. It was also more for crystallization experiments recorded at high temperatures.

To determine the reproducibility of our data, a second sample of hyperquenched glassy (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water was prepared and its crystallization also studied at 144 K. The resolved peak heights and their variation with time for crystallization was within  $\pm 2\%$  of the corresponding values for the first sample.

Because areas of the bands due to the crystalline ice fraction are directly proportional to the peak height (which was checked for the ice bands shown in Fig. 2 and for that corresponding to a completely crystallized state), the ratio of the peak height at time  $t$  to that at the completion of crystallization,  $I(t)/I(\infty)$ , is equal to the fraction of water,  $x$ , crystallized at time  $t$ . This procedure also represents a normalization of the data.  $x$  was calculated for both sets of measurements of unannealed samples at 144 K (right curve) and is plotted against the logarithmic time in Fig. 3. The combined error in the measurement and analysis is shown. Evidently,  $x$  for the two samples agrees within the error limits.

A new sample of hyperquenched glassy (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water was prepared for determining the effect of annealing on its crystallization kinetics. As in our earlier

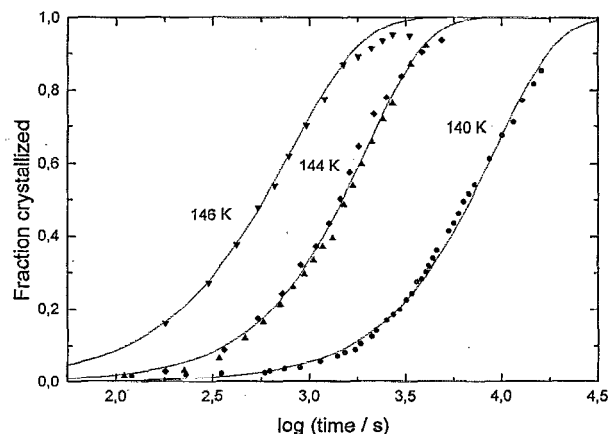


FIG. 4. The fraction of water crystallized at various temperatures is plotted against the logarithmic time at the indicated temperatures. Smooth lines through the data points are for the calculated values from Eq. (1) using the values of  $k$  (converted to units in  $\text{s}^{-n}$ ) and  $n$  given in Table I. For 144 K data points of two independently prepared samples are shown. The samples are distinguished by  $\Delta$  and  $\blacklozenge$ .

studies of the glass transition behavior,<sup>1,2</sup> it was annealed for 120 min at 130 K. During this period the shape of the IR spectrum of the sample did not change. It was then heated to 144 K and the IR spectrum measured at different times during its crystallization. The data were converted to values of  $x$ , which is also plotted in Fig. 3, which shows that annealing of the sample below its  $T_g$  of 136 K causes a considerable increase in both the fraction crystallized at time  $t$  and the rate of crystallization.

Two more samples of hyperquenched glassy (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water were prepared and their crystallization kinetics studied at 140 K, and 146 K. The calculated  $x$  for different temperatures is plotted against the logarithmic time in Fig. 4.

#### IV. DISCUSSION

According to the theory of phase transformation by nucleation and growth, a generalized expression for the fraction transformed is<sup>11-13</sup>

$$x = 1 - \exp(-kt^n), \quad (1)$$

where  $k$  is the rate constant, and  $n$  is a parameter whose magnitude is determined by the geometry of the growing particles and whether the transformation is interface or diffusion controlled. For an interface-controlled transformation,  $n$  is an integer from 1 to 4, depending upon the shape of the particle. For a diffusion-controlled transformation,  $n$  is usually a fraction except for the cylindrical geometry of the particle when it is equal to 1. When the nucleation rate is high and the growing particles spherical,  $n=1.5$ . Thus, the nature of crystallization kinetics can be judged from the knowledge of the parameter  $n$ .<sup>12,13</sup>

Equation (1) may be written as

$$\ln[-\ln(1-x)] = \ln k + n \ln t. \quad (2)$$

Thus, a plot of  $\ln[-\ln(1-x)]$  against  $\ln t$  is linear from which  $k$  and  $n$  can be determined. A typical plot for

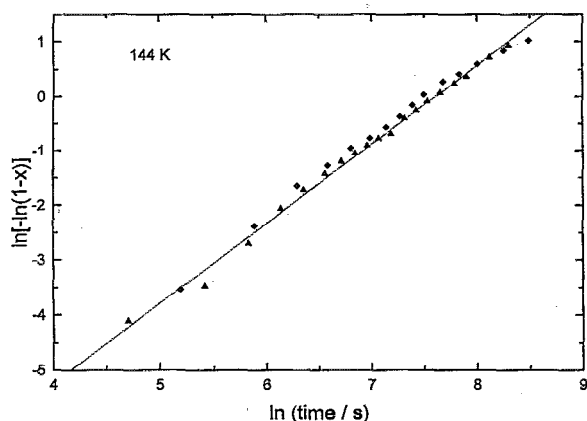


FIG. 5. A plot of  $\ln[-\ln(1-x)]$  against the logarithmic time for two independently prepared samples of water kept at 144 K. The samples are distinguished by  $\Delta$  and  $\bullet$ . Using Eq. (2) this gives values of  $k=3.9 \times 10^{-5}$  and  $n=1.34$ .

the crystallization of water at 144 K is shown in Fig. 5, which gives  $k=3.9(\pm 0.6) \times 10^{-5} \text{ s}^{-n}$  and  $n=1.34 \pm 0.02$ . From these values and Eq. (1),  $x$  was recalculated and its variation with time is shown by the smooth line in Figs. 3 and 4. Data for other temperatures were analyzed similarly and the calculated values of  $x$  drawn in Fig. 4. Values of  $k$  and  $n$  for different temperatures are listed in Table I. These values of  $n$  are within  $\pm 15\%$  of 1.5.

According to the criteria for the values of  $n_{13,14}$  the crystallization kinetics of water to cubic ice at  $T < 150 \text{ K}$  is diffusion controlled with particles growing into a predominantly spherical geometry. Strictly speaking,  $n=1.5$  when nucleation is nearly completed before the growth begins or when the nucleation rate in the latter stages of growth is negligibly small.<sup>12,13</sup> Any departure from this value is a reflection of change in the morphology of the particles and/or significantly high nucleation rate throughout the duration of crystallization.

When  $n$  in Eq. (1) does not change with temperature, the rate constant is written as

$$k = k_0 \exp(-\Delta H/RT), \quad (3)$$

where  $k_0$  is the pre-exponential factor and  $\Delta H$  the appropriate activation energy.  $k$  and  $k_0$  are in  $\text{s}^{-n}$  units. But since  $n$  changes with temperature,  $k$  and  $k_0$  need be expressed in units of  $\text{s}^{-1}$ , so that,

TABLE I. The parameters for crystallization of hyperquenched glassy (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water at different temperatures.

Temperature (K)	$n$	$k (\text{s}^{-1})^a$	$t_{\max} (\text{s})^b$
140	1.30	$1.1 \times 10^{-4}$	$3.0 \times 10^3$
144	1.34	$5.1 \times 10^{-4}$	$7.0 \times 10^2$
146	1.15	$1.2 \times 10^{-3}$	$1.4 \times 10^2$
144 annealed	2.43	$1.4 \times 10^{-3}$	
	0.90	$8.4 \times 10^{-4}$	

<sup>a</sup> $k$  is the rate constant and  $n$  a parameter defined for Eq. (1).

<sup>b</sup> $t_{\max}$  is the time where the rate of crystallization has reached its maximal value for a given temperature.

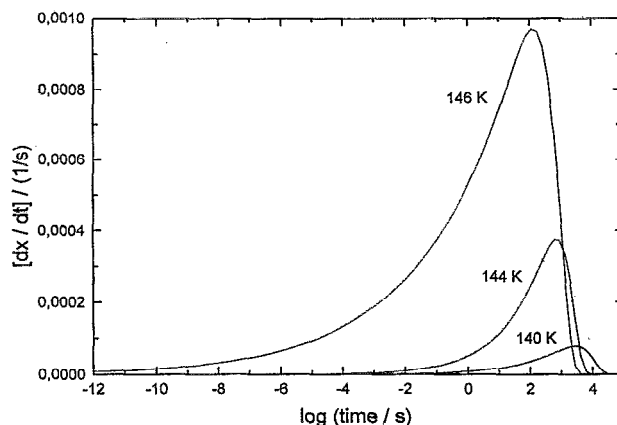


FIG. 6. The crystallization rate of metastable (2 wt %  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) water at different temperatures is plotted against the logarithmic time. The curves are calculated from Eq. (6) using the values of  $k$  (converted to units in  $\text{s}^{-n}$ ) and  $n$  given in Table I.

$$(k)^{1/n} = (k_0)^{1/n} \exp(-\Delta H^*/RT), \quad (4)$$

where  $k$  and  $k_0$  in Eq. (4) are now in units of  $\text{s}^{-1}$ . According to Eq. (4), a plot of  $\ln[(k)^{1/n}]$  against  $1/T$  would be close to a straight line [not strictly a straight line because the intercept  $(k_0)^{1/n}$  changes with  $T$  through  $n$ ]. From this plot, we obtain  $\Delta H^* = 67 \pm 3 \text{ kJ/mol}$ . When a liquid crystallizes at low temperatures, the crystal growth rate is limited by the viscosity of the liquid. In this instance,  $\Delta H^*$  can be interpreted as the activation energy for viscous flow.

From Eq. (1), the isothermal crystallization rate is given by

$$\partial x / \partial t = kn t^{n-1} \exp(-k t^n). \quad (5)$$

Therefore,  $(\partial x / \partial t)$ , when plotted against time, will show a peak at

$$t_{\max} = [(n-1)/kn]^{1/n}. \quad (6)$$

Plots of  $(\partial x / \partial t)$  against the logarithmic time are shown in Fig. 6, which show a peak as required by Eq. (6), which may be written as

$$\ln t_{\max} = \ln[(n-1)/n]^{1/n} - (1/n) \ln k_0 + \Delta H^*/RT \quad (7)$$

so that for a constant value of  $n$  with changing temperature,  $\ln t_{\max}$  would increase linearly with  $1/T$ , with the same  $\Delta H^*$  as in Eq. (4). The self-consistency of Eqs. (4) and (7) may be useful in further investigations of glassy water's crystallization under various conditions and in determining the predominant mechanisms of crystallization.

Finally, we consider the effect of sub- $T_g$  annealing on the crystallization kinetics of metastable water at 144 K, as is seen in Fig. 3. Annealing densifies most glasses as the crystals of most substances are denser than their liquids. Water is an exception to it and, since its coefficient of thermal expansion is negative below 273 K, its annealing is expected to decrease its density. Annealing below  $T_g$  also allows the crystal nuclei formed during the hyperquenching to grow at a slow rate, or any microcrystals formed to

grow into grains. When this has occurred and the glassy water is thereafter heated to  $T > T_g$ , the crystallization kinetics as measured by FTIR spectroscopy or other methods at a temperature  $T$  would show characteristics different from the usual nucleation and growth process. Although Eq. (1) would still describe the kinetic processes, the parameter  $n$  would not be 1.5. With this in view, the data at 144 K obtained for the annealed glassy water were fitted to Eq. (1) to two processes, as shown by the lines in Fig. 3. (This was also necessary since no set of  $k$  and  $n$  parameters for a single process could describe the data.) During the early stage of the crystallization kinetics,  $n=2.43$  and  $k=1.4 \times 10^{-3} \text{ s}^{-1}$ . This  $n$  value is close 2.5 expected for diffusion controlled growth of spherical nuclei which may have formed during the annealing. As crystallization progressed this kinetics changed gradually to one described by the parameters  $n=0.90$  and  $k=8.4 \times 10^{-4} \text{ s}^{-1}$ , which is attributed to diffusion-controlled growth of cylindrical nuclei growing radially<sup>13,14</sup> (strictly speaking,  $n=1$ , for this case). The fit of the data to Eq. (1) seems satisfactory. But direct microscopic observations of the transforming substance as a function of time, as is required for most such studies, are necessary before reaching definite conclusions on the morphology of the growing particles.

These results show also the scope of FTIR spectroscopy for examining crystallization of metastable liquids at

temperatures when both nucleation and growth of the crystal phase become diffusion controlled.

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