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Small-angle x-ray scattering in the early stages of ice formation

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The freezing of supercooled water is measured at the small-angle x-ray facilities at the Synchrotron Radiation Source in Daresbury, United Kingdom, for $0.1 \text{ nm}^{-1} < \mathbf{k} < 2 \text{ nm}^{-1}$ in the temperature range from 250 to 273 K. A sharp peak in the spectra of ice is observed at a scattering wave-vector value given by $\frac{1}{8}(1-\delta)$ times a reciprocal-lattice vector of the hexagonal or cubic ice. The mismatch δ decreases in time after the onset of freezing and vanishes after about two hours just as the intensity does. A possible explanation in terms of a growth mechanism is discussed.

INTRODUCTION

When water contained in a glass capillary is cooled below its normal melting point it will freeze at temperatures anywhere between 260 and 240 K [1]. Such degrees of supercooling lead to a very rapid polycrystallization. Simple observation with a CCD camera shows an event developing in time with a speed on the order of 10–100 cm/sec. Such speeds are in agreement with determinations of the velocity of proceeding ice-water interfaces under similar conditions by Hillig and Turnbull [2]. These authors noted that the growth of ice from supercooled water enclosed in a tube is not simply controlled by dissipation of the latent heat, but by a specific growth mechanism that limits the speed of growth considerably. It has been suggested that growth proceeds by a screw dislocation mechanism which severely restricts the fraction of the total sites on the crystal surface that is available for attachment of new molecules. In any case it is clear that the dynamics of crystal growth involves the diffusion of latent heat as well as the ordering of molecules.

More recently experiments have been reported on a growing ice crystal in a stationary situation which involves a much smaller supercooling. Light scattering from the ice-water interface shows a strong anomalous scattering at high growth rates [3,4]. Above the threshold growth rate the scattering intensity increases linearly with the growth rate but exhibits hysteresis so that the excess scattering persists when the growth rate is reduced to below the critical rate. Furthermore the intensity-intensity correlation function decays with a characteristic time Γ^{-1} where Γ depends quadratically on the scattering vector $\mathbf{k}$, $\Gamma = D_s k^2$ with D_s independent of the growth velocity and on the order of $3 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$.

These experiments have led to a discussion about the interpretation of the origin of the anomalous scattering from which two points of view emerged.

The scattering could arise from an interface layer of a thickness on the order of $5 \mu\text{m}$ with properties distinctly different from those of ice or water. The diffusion coefficient D_s , which is very small compared with the

thermal diffusion coefficient of water, would then be associated with entropy fluctuations involving order and disorder with respect to the sites as well as to the orientation of molecules in the interface layer [5].

On the other hand, it has been pointed out that the observed properties could also be explained by assuming that the anomalous scattering arises from scattering in the solid phase [6]. At the growing interface defects are created at a rate that depends on the growth velocity. The growth may be effectuated by two mechanisms, one which is independent of dislocations at the surface and one that depends on the presence of dislocations, in particular spiral dislocations. The interplay of the concentration of simple point defects that may give rise to large-scale dislocations, concentration of dislocations, and growth rate, constitutes a layer of defects on the crystal side of the growing interface which might give rise to excess light scattering once a critical growth rate is surpassed. The diffusion constant D_s is in this view related with the diffusion of the defects in the crystal at the growing interface as discussed by Keizer, Mazur, and Morita [7].

Experiments to test the correctness of either of the two starting points have been suggested but the use of visible light which makes accessible scattering vectors of about 10^{-2} nm^{-1} may not quite be the best choice to probe for the role of structures on the order of 1–10 nm. Small-angle x-ray scattering might be a better choice with access to scattering wave vectors between 10^{-1} and 30 nm^{-1} . On the other hand, the use of x rays excludes experiments so carefully designed as the light scattering experiments by Böni, Bilgram, and Känzig [3]. We therefore had to content ourselves with simple x-ray scattering measurements on a thin walled capillary tube filled with water and cooled from the outside.

EXPERIMENT

The experiments were performed at the Synchrotron Radiation Source at Daresbury, U. K.

The intensity of the photon beam is on the order of 10^{11} photons/sec with a photon wavelength of $1.5 \text{ \AA}$. The monochromatic beam in our experiments had a

width of 4 mm and a height of 0.3 mm. The absorbance in the cell and the total intensity of the photon beam during an experiment were monitored by two ionization type detectors. One was placed in front and one behind the sample cell. This enabled us to detect the freezing of the supercooled water.

The scattering intensity was measured by a quadrant detector. The sensitivity of this type of detector is much greater than that of the linear detector used in our previous experiments [6] and gives an improvement of the signal-to-noise ratio of several orders. The distance between sample cell and detector was 450 cm; the wave vector measured was from 0.1 to 2 nm⁻¹. Experiments on wet collagen were used to calibrate the wave-vector scale. The water samples were contained in a capillary made from Lindemann glass. These capillaries were flattened in a carbon mould so that a cross section of 5 by 10 mm² was obtained. That allowed us to use the capillaries in a vertical as well as in a horizontal position. The optical path length was 1 mm and the wall thickness 0.01 mm.

The cooling of the samples was done by Peltier elements via heat pipes. The sample was surrounded by a cooled silver block to minimize temperature gradients.

The water used was carefully cleaned, double distilled, deionized, and filtered through a 0.1- μ m membrane filter. After degassing it was distilled in a carefully cleaned glass container, which was sealed off. This container was opened immediately before the experiment when the water was put into the capillary via a syringe.

RESULTS

Figure 1 shows a typical example of the wave-vector dependence of the scattered x-ray intensity for a water

FIG. 1. X-ray scattering intensity as a function of scattering vector and temperature, after subtraction of the scattering intensity of the sample at 273 K. The arrow at 256 K (-17°C) indicates the run during which the sample froze.

sample that is slowly lowered in temperature. The scattering from the sample at 273 K is subtracted from all the spectra. The duration of the successive runs is 700 sec; the particular sample started to freeze during a run taken at -17°C . The increase of scattering intensity with decreasing temperature in the supercooled water phase is virtually independent of the wave vector and is in accordance with the increase of the isothermal compressibility over this temperature range [8]. Freezing of the sample is detected by the heat release, the thermal relaxation time of the sample is about 100 sec, and because of the large heat capacity and high thermal conductivity of the silver housing temperature equilibrium is rapidly restored. In the subsequent ice phase runs it is seen that besides a high peak at $k=0$ (partly due to secondary emission from the beam stop) several distinct smaller peaks at finite wave vector grow and disappear again. Although the relative intensities of these peaks vary in repeated experiments the wave-vector values at which these peaks appear are very reproducible; recent values are $k=1.07$, 0.54 , and 0.34 nm⁻¹. In many cases the peak at $k=1.07$ nm⁻¹ is so pronounced that we could establish that the intensity and the exact value of the wave vector of maximum intensity is a function of time rather than a function of temperature. This is illustrated in Figs. 2–4. From Fig. 2 it can be concluded that the width of the peak is not more than 0.05 nm⁻¹, indicating a correlation length of at least 20 nm. Figure 3 shows growth and decay of the peak intensity matching two consecutive first-order mechanisms with relaxation times of about 700 and 200 sec, respectively. Figure 4 shows the wave-vector shift with time where the obviously incommensurate wave vector is expressed as $k_{\delta} = \frac{1}{8}(1-\delta)c^*$, where c^* is the reciprocal-lattice vector in the [111] direction in the cubic I_c ice of a length of 0.734 nm corresponding with the basis vector c in hexagonal ice [9]. The peaks that appear at smaller wave vectors are much less intense and do not allow a quantitative

FIG. 2. The superstructure peak at $k=1.07$ nm⁻¹ measured in successive experimental runs of 700 sec.

FIG. 3. The relative peak intensity of the superstructure peak of Fig. 2 as a function of time.

FIG. 4. The mismatch δ of the superstructure peak as a function of time. The steps in the δ values are caused by the limited resolution of the detector.

determination of intensity and wave-vector shift with time. Quantitatively the wave vectors can be characterized by $\frac{1}{16}c^*$ and $\frac{1}{24}c^*$.

DISCUSSION

The superlattice reflections that we find in the early stages of ice formation indicate that the superlattice structures have a unit-cell dimension of approximately eight or multiples of eight times longer than in the equilibrium phase. We also find that at least the satellite reflection at $k_{1/8} \approx 1/8c^*$ is well described by $k_\delta = (1/8)(1-\delta)c^*$ with δ changing in time from 0.03 in the first ten minutes after solidification of the sample to zero after about three hours. The freshly grown ice has clearly an incommensurably modulated structure which anneals to form a perfect ice crystal. It is to be noted that the variation of the wave-vector value in time considerably exceeds any possible variation due to thermal expansion and also is much larger than the difference between the corresponding lattice vectors in hexagonal and cubic ice (0.734 and 0.731 nm, respectively). Because of the limited resolution of the experiment, the determination of the wave vector of maximum scattering alone would not allow the choice between the lattice vectors of the two ice forms. However, the total disappearance of the intensity (Fig. 3) at a time when the wave vector versus time function has not yet reached the value appropriate for hexagonal ice made us tentatively choose the value for cubic ice of c^* (Fig. 4). No superstructure peaks should appear for $\delta=0$; a commensurate modulation is not expected.

The factor 8 that appears in the superstructure may at first seem puzzling. It may be introduced by screw dislocations of quasirhombic symmetry. The pitch of such dislocations is such that rotation over 2π in the plane perpendicular to the c axis ([111] axis as the case may be) gives a distance of eight times the repeat distance along that axis. If this surmise were true one could imagine the following succession of events at the sudden freezing of the deeply supercooled water samples. From a first nucleus, heterogeneous at the wall or formed by a chance process in surface layer turbulence an ice surface starts to grow in the direction of the c axis with a spiral dislocation mechanism where the spirals have quasirhombic symmetry. Since the solidification and reestablishment of thermal equilibrium proceeds much faster than the defects can diffuse away, a crystal with many screw dislocations is formed. The pitch of eight in the direction of the c axis introduces a slightly incommensurate periodicity of multiples of about eight repeat distances. The defects diffuse away into the crystal with a diffusion constant $D \approx 100 \mu\text{m}^2 \text{sec}^{-1}$ [10] which gives a relaxation time of about 2000 sec and disappear finally by annealing. This picture would be in agreement with the main points of our experimental findings, viz., the wave-vector value of the superstructure peaks, the rate at which these peaks appear and disappear, and the minimum correlation

length of the structures.

Finally one can doubt the relevancy of the difference between the hexagonal I_h structure and the cubic I_c structure in connection with the ephemeral ice structures with a very high concentration of lattice defects. The perturbing influence of the proximity of a wall alone can favor the crystallization of cubic instead of hexagonal ice [11]. Our experimental findings may hence be interpreted as a confirmation for the mechanism of ice growth.

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- [1] *Water, A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1982), Vol. VII.
 - [2] W. B. H. Hillig and D. T. Turnbull, *J. Chem. Phys.* **24**, 914 (1956).
 - [3] P. Böni, J. H. Bilgram, and W. Känzig, *Phys. Rev. A* **28**, 2953 (1983).
 - [4] J. P. Vesenka and Y. Yeh, *Phys. Rev. A* **38**, 5310 (1988).
 - [5] J. H. Bilgram, *Phys. Rep.* **153**, 1 (1987).
 - [6] J. C. F. Michielsen, A. Bot, and J. van der Elsken, *Phys. Rev. A* **38**, 6493 (1988).
 - [7] J. Keizer, P. Mazur, and T. Morita, *Phys. Rev. A* **32**, 2944 (1985).
 - [8] R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).
 - [9] N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge University Press, Cambridge, 1970).
 - [10] K. Gato, T. Hondoh, and A. Higashi, *Point Defects and Interactions in Metals* (University of Tokyo Press, Tokyo, 1982).
 - [11] D. C. Steytler, J. C. Dore, and C. J. Wright, *J. Chem. Phys.* **87**, 2458 (1983).