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ELLIPSOMETRIC STUDY OF THE ICE SURFACE STRUCTURE JUST BELOW THE MELTING POINT

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Résumé - L'indice de réfraction n_1 et l'épaisseur de la couche de transition (Q.L.L.) à la surface d'un cristal de glace à température juste en-dessous du point de fusion (0°C) ont été mesurés à l'équilibre en utilisant une méthode d'ellipsométrie in-situ. Les couches de transition ont été observées à des températures supérieures à -2 et -4°C pour les faces {0001} et {10$\bar{1}$0} respectivement et n_1 = 1,330 pour les deux faces. Cette valeur est très proche de celle de l'eau en volume à 0°C. Associé à des observations sur les formes des cristaux de glace près du point de fusion, on doit s'attendre à ce que la structure de l'interface entre la couche de transition et la glace sur la face {10$\bar{1}$0} varie brutalement au-dessous de -2°C pour devenir plus rugueuse.

Abstract : The refractive index n_1 and the thickness d of the transition layer (quasi-liquid layer) on the surface of an ice crystal at temperatures just below the melting point (0°C) were measured in equilibrium, using an in-situ method of ellipsometry. The transition layers were observed at temperatures above -2 and -4°C for {0001}- and {10$\bar{1}$0}-faces, respectively, and n_1 was 1.330 for both faces, which is very close to the refractive index of bulk water at 0°C (n_w=1.333). Combined with the observational results about the ice crystal shapes near the melting point, it was expected that the interface structure between transition layer and ice on the {10$\bar{1}$0}-face changes from smooth to rough at -2°C.

1. Introduction

It is known that the ice crystal surface is covered with a transition layer (so-called quasi-liquid layer, hereafter QLL) at temperatures just below its bulk melting point (0°C) in equilibrium. The surface structure like this is intimately related to the physical phenomena such as the mechanical adhesion[1,2], sintering[3], gas adsorption[4,5], dielectric constant[6], surface electrical conductivity[7,8], NMR[9], Volta effect[10], photoemission[11] and surface disorder[12]. Although these experimental results show the existence of the transition layer on the ice surface, conclusions differ each other on the physical properties of the layer, its thickness and the temperature range for which it is stable. Recently, Beaglehole and Nason[13] showed, by the measurements of the ellipticity coefficient for the reflected light from the ice surface, that the layer thickness depends on the surface orientations. We consider, however, that there were some problems in their measurements; first they assumed that the refractive index of the transition layer was equall to that of bulk water, and second the ice surfaces used were prepared destructively. Consequently, we do not know yet whether the transition layer on the ice surface is "water-like" indeed and how thick it is.

On the other hand, several theoretical works about the transition layer have been published. Fletcher[14] indicated that the water layer is energetically favored at temperatures above -(5 ± 3)°C and its thickness decreases with decreasing temperature. Kuroda and Lacmann[15] showed that the QLL on the ice surface is thermodynamically stable above a critical temperature and the habit change of snow crystals can be explained by the anisotropy of the thickness of QLL.

The aim of this work is to measure directly the physical properties and the thickness of the transition layer on {0001}- and {10$\bar{1}$0}-faces of ice single crystal, using an ellipsometry. As a result, the temperature dependence and the anisotropy of the layer thickness are clarified and the surface structure of ice crystal is discussed in connection with the habit change of ice crystals observed just below the melting point.

2. Experimental

2.1 Ellipsometry

When the linearly polarized light is reflected at the surface covered with the transition layer like QLL (fig. 1), it is changed to the elliptically polarized light. Then the complex relative amplitude attenuation ρ, which is a ratio of amplitude reflectivities (R_p and R_s) of p- and s-polarizations, is given by,

$$\rho = R_p/R_s = \tan\Psi \exp(i\Delta) \qquad (1)$$

Where, $\tan\Psi$ is related to the relative amplitude change and Δ to the relative phase change. The value ρ is extremely sensitive to the refractive index n_1 and the thickness d of the layer[16].

A null ellipsometry was operated for the He-Ne laser beam (λ=633nm) in a walk-in cold room. To measure ρ of ice surface at maximum sensitivity to n_1 and d, the angle of incidence ϕ_0 was set to 52.950°. The sample was put in a chamber with two small holes to admit the laser beam. The inside wall of the sample chamber was covered with a thin ice sheet which works as a vapor source. Temperatures of sample and vapor source were able to be controlled separately.

2.2 Sample of ice surface

The sample of ice surface used in this experiment was a slice of a negative crystal (fig. 2-a), which is a hole in a shape of a sharp hexagonal prism grown at the end of a hypodermic needle inserted in an ice single crystal, by continuous evacuation of water vapor through the needle[17,18]. The surface prepared in this way has several characteristics as follows; (1) the maximum diameter of surface is

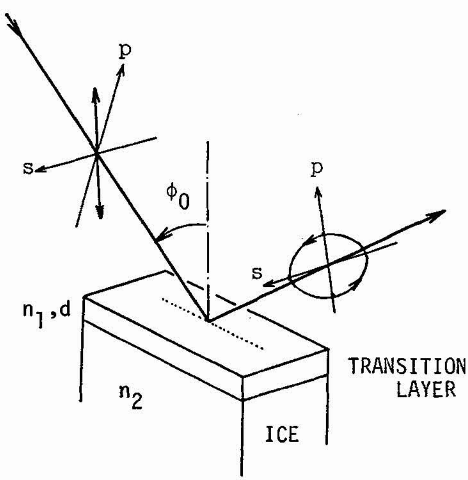

Fig. 1 Schematic illustration of the reflection of polarized light at the surface covered with a transition layer. n_1, n_2: refractive indices of the transition layer and ice, d: thickness of the layer. The p-polarization is parallel to the plane of incidence and the s-polarization perpendicular to the surface.

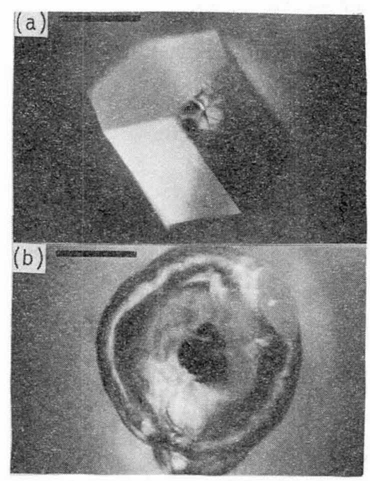

Fig. 2 Negative crystals of ice: (a) a negative crystal with a hexagonal prism shape (below -2°C); (b) a spherical negative crystal with two small basal facets (above -2°C). Scale bars indicate 1 mm.

3 to 4 mm, (2) molecularly flat, (3) free from misorientations (exact surface orientation of {0001} and $\{10\bar{1}0\}$), and (4) free from contaminations. Consequently, these surfaces are the best one in the purpose of the investigation of crystal surface.

3. Experimental results

A series of experiments were carried out at various conditions. For all experiments, the surface temperature T_S was set first below -10°C, and increased at the constant rate of 0.1°C/min or less.

Figure 3 shows the typical change of observed (Ψ, Δ) at the condition close to the equilibrium, which is plotted in a polar coordinate (Ψ, Δ). The thin solid curves show simulated changes in ρ for thickening a single layer of various refractive indices. When the transition layer does not exist on the surface, (Ψ, Δ) is plotted at the point S. Since the refractive index of bulk water is 1.333 at 0°C, a change in n_1 appears mainly in Ψ, whereas d appears in Δ, if the layer is water-like. The observed changes of (Ψ, Δ) for {0001}- and $\{10\bar{1}0\}$-faces show that the refractive index of the transition layer is around 1.330, which is quite close to that of water. It also means that the properties of the transition layer are water-like and the single layer model is acceptable for the model of ice surface structure.

Figure 4 shows the change in Δ with respect to T_S for both faces. Under the conclusion that the refractive index of the transition layer is 1.330, the change of Δ can be read as the change of the layer thickness as shown in fig. 4. This results show that the temperature T_W, at which the QLL appears on the ice surface, is -2°C and -4°C for {0001}- and $\{10\bar{1}0\}$-faces, respectively. Although the temperature dependence of d and the temperature T_w for $\{10\bar{1}0\}$-faces fairly scattered from sample to sample, systematic differences in d and T_w between both faces were confirmed by a series of experiments.

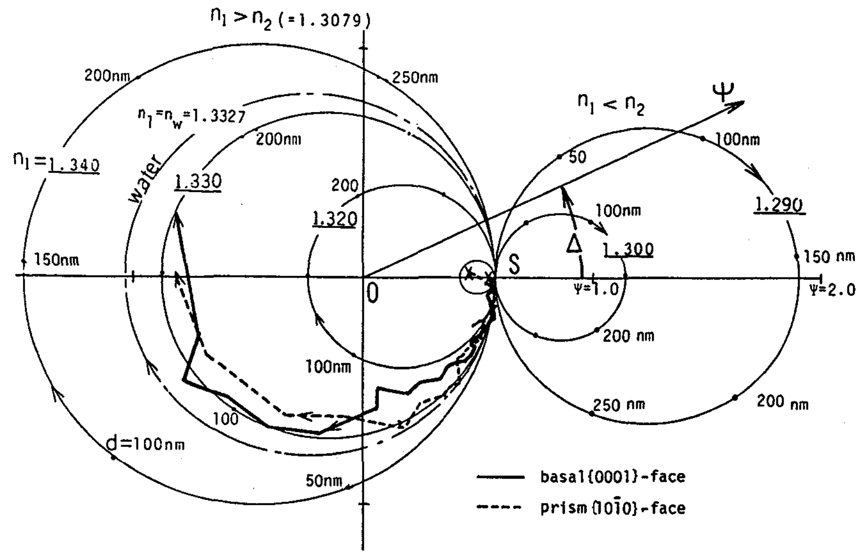

Fig. 3 Observed changes of $\rho = \tan\Psi \exp(i\Delta)$ in a polar coordinate (Ψ, Δ) for {0001}-face (solid line) and $\{10\bar{1}0\}$-face (broken line) with increasing temperature, and simulated changes of ρ for thickening layer (thin solid curves) with various refractive indices n_1 on ice. Crossed marks show the starting points of experiments.

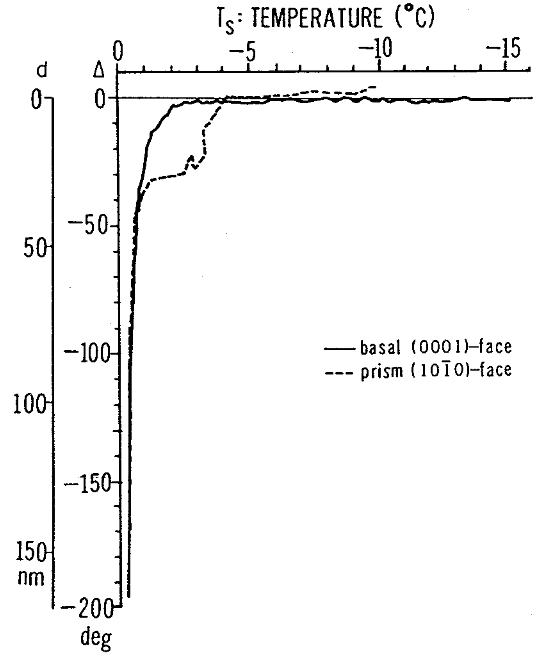

Fig. 4 Temeprature dependence of Δ and the thickness change of the transition layer under the conclusion of n_1=1.330.

4. Discussion

Kuroda and Lacmann[15] theoretically discussed the temperature dependence and anisotropy of the thickness of QLL as follows.

The existence of QLL on the ice surface is disadvantageous due to the bulk free energy of the liquid phase. However, it lowers the surface free energy of the system, so that it is to be possible that the QLL stably exists on the surface. For ice surface covered with QLL, they indicated that the wettability parameter $\Delta\sigma_\infty$ becomes plus value. That is,

$$\Delta\sigma_\infty = \sigma_I - (\sigma_W + \sigma_{I/W}) > 0 \qquad (2)$$

where σ_I, σ_W and $\sigma_{I/W}$ are the surface free energies per unit area (surface tension) for the interface of vapor/ice, vapor/water and ice/water, respectively. Consequently, the equilibrium thickness of QLL d_{eq} is determined by the balance between the disadvantage of the bulk free energy and the fall of the surface free energy.

$$d_{eq} = -A + \left[\frac{n\, A^n\, \Delta\sigma_\infty\, V_m\, T_m}{Q_m\, \Delta T} \right]^{1/(n+1)} \qquad (3)$$

where n and A are parameters connected to the interaction between water molecules, V_m the molecular volume, T_m the melting temperature of ice, ΔT the supercooling and Q_m the latent heat of fusion per molecule.

From the equation (2) and (3), d_{eq} increases with increasing $\Delta\sigma_\infty$. As the surface energy per unit area is proportional to the number density of broken hydrogen bonds along the surface (broken bond model), $\sigma_I(0001) < \sigma_I(10\bar{1}0)$. Consequently, the following relation is expected,

$$\Delta\sigma_\infty(0001) < \Delta\sigma_\infty(10\bar{1}0) \rightarrow d_{eq}(0001) < d_{eq}(10\bar{1}0)$$

$$\rightarrow T_w(0001) > T_w(10\bar{1}0) \qquad (4)$$

In the present experiment, it is clarified that $T_W(0001) > T_W(10\bar{1}0)$ and the thickness increases with increasing temperature. These results qualitatively coincide with the theoretical explanation by Kuroda and Lacmann[15].

The temperatures when the QLL appears on the ice surface are higher than those temperatures which have been obtained by other experiments. This reason is considered that the surfaces used in the present experiment were molecularly flat and free from misorientations and contaminations, compared with the rough and high index surfaces used in other experiments. Because σ_I for the rough and high index surface is higher than $\sigma_I(0001)$ or $\sigma_I(10\bar{1}0)$, surfaces like this are more wettable than {0001}- and {10$\bar{1}$0}-faces (namely, $T_w(0001) > T_w(10\bar{1}0) > T_w$(high index)).

On the other hand, it has been clarified that the conspicuous habit change of ice crystal occurs at the temperature of -2°C (fig. 5). Kohata et al.[18] showed that the shape of negative crystal (evaporation form) changes to the sphere which is truncated with only small {0001}-facets above -2°C (fig. 2-b), compared with the hexagonal prism surrounded by both {0001}- and {10$\bar{1}$0}-facets below -2°C (fig 2-a). Yamashita and Asano[19] showed that the shape of snow crystal (growth form) also changes from the hexagonal plate to the circular disk above -2°C. These observational results mean that the anisotropy of growth or evaporation rates with respect to all surfaces with crystallographic orientations excepting {0001} disappears at temperatures above -2°C. The disappearance of anisotropy like this may occur when the differences of surface structures are vanished by the occurence of surface roughening.

The present experimental results showed that the {10$\bar{1}$0}-face is covered with QLL at temperatures above -4 °C. Consequently, we should consider that the interface structure between QLL and ice changes from smooth to rough above -2°C for the {10$\bar{1}$0}-face, though the interface on {0001}-face is kept smooth at whole temperature range (0 to -2°C). That is, the surface roughening occurs for the interface on the {10$\bar{1}$0}-face at this temperature.

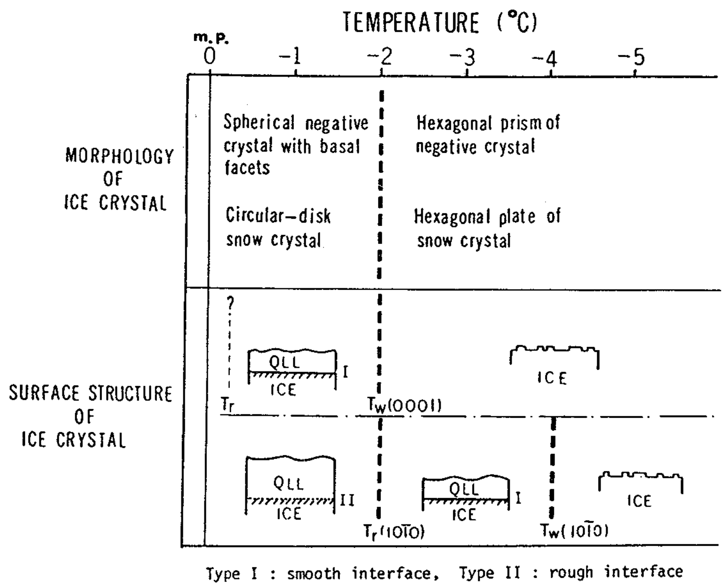

Fig. 5 Schematic diagram to show the relation between the microscopic surface structure and the ice crystal morphology. T_r is the temperature at which the surface roughening transition occurs.

5. Conclusions

The conclusions obtained in this study are summarized as follows:

1) The refractive index of the transition layer is 1.330 for {0001}- and {10$\bar{1}$0}-faces, which means the properties of the transition layer are very close to those of bulk water(n_w=1.333); that is to say, the transition layer is QLL.
2) $T_w(0001) = -2°C$ and $T_w(10\bar{1}0) = -2\sim-4°C$. The thickness of the transition layer increases with increasing temperature and $d_{eq}(0001) < d_{eq}(10\bar{1}0)$ at temperatures above -4°C.
3) These experimental results are qualitatively explained by the theory of Kuroda and Lacmann[15].
4) The habit change observed for the negative crystal and the snow crystal indicates that the surface roughening occurs at the interface between QLL and ice crystal on the {10$\bar{1}$0}-face at the temperature of -2°C.

6. Acknowledgements

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7. References

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COMMENTS

V.F. PETRENKO

When you calculate the thickness of a liquid layer you imply that it is a homogeneous one. But if it is not, does this change your results ?

Answer :

We can also obtain the simulated diagram of ($\Psi.\Delta$) for the inhomogeneous or multilayers model. But their diagrams completely differ from that for the homogeneous single layer model. Experimental data obtained in this experiment show the best fitting to the diagram for the homogeneous single layer model. Consequently, we should consider that the QLL is the homogeneous single layer.