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X-RAY DIFFRACTION PATTERN OF QUASI-LIQUID LAYER ON ICE CRYSTAL SURFACE

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Abstract: The existence of a quasi-liquid layer on the surface of ice crystals at temperatures not far below 0°C is widely accepted on the basis of many experimental and theoretical studies (e.g., 1-4). However, there has been no experimental study including the direct information on the structure of the quasi-liquid layer. It is therefore highly desirable to obtain structural data by X-ray diffraction method. In this study, we investigated the dependence on temperature of the X-ray diffraction pattern of the surface of ice crystals and obtained direct evidence that there was no long range order of the structure in the quasi-liquid layer on ice surface near 0°C.

In general, it is difficult to obtain clear X-ray diffraction pattern of thin film on a substrate. We get only obscure diffraction pattern by usual 2θ/θ scan diffractometer, because the diffraction pattern of thin film is disturbed by strong diffracted beam from the substrate crystal. So, usual diffractometer was remodeled for the study of thin films (Rigaku TFD System). To increase an intensity of diffracted X-ray from the thin film, we kept an incidental angle at a fixed value, e.g., 2 degree, during measurement, and scanned only X axis. We used a Soller slit and a platy graphite monochromator, to increase angular resolution of diffracted X-ray and signal to noise ratio, respectively. The specimen holder which contained ice crystals was mounted on the diffractometer. We can control both surface temperature of ice crystal and supersaturation independently. We used both ice single crystals and polycrystals whose surface was smoothened by microtome. The diffraction pattern of ice crystal surface under the equilibrium condition was measured between -0.5 and -10°C with the use of CuKα1 X-rays.

Figure 1 shows an example of X-ray diffraction patterns of the polycrystal ice surface obtained at -7.3, -2.1 and -1.1°C. There are some diffraction peaks of ice Ih at -7.3°C (Fig. 1a), even though the pattern does not coincide with ideal powder diffraction pattern, because grain sizes are large about 2 mm in diameter. It is noted that intensity of some peaks of the ice Ih at -2.1°C (Fig. 1b) are relatively weak in comparison with those of -7.3°C (1a). These results are interpreted as follows. The thickness of the quasi-liquid layer increases with increasing temperature (2-4). Therefore, the diffraction of the ice Ih are weakened by the thicker quasi-liquid layer on ice surface at -2.1°C. In Fig. 1c, the pattern at -1.1°C contains a diffraction halo centered at 2θ ~ 26° in addition to the weak reflexes of the ice Ih, which clearly indicates that there is no long range order of the structure in the quasi-liquid layer. This is a first clear evidence that the so-called "quasi-liquid layer" is a liquid layer. Again the diffraction peaks of the ice Ih are more weakened compared with Fig. 1b. Same results were obtained when single crystals were used.
Figure 2 shows the change in intensity of diffraction halo at $2\theta = 28^\circ$ as a function of temperature. The intensity, which is proportional to the thickness of the quasi-liquid layer, increased with temperature. This is qualitatively consistent with the theory of Kuroda & Lamm (4) and with the ellipsometric observation (2). However, no difference was observed between polycrystalline and single ice crystals and between (0001) and (1010) faces in the intensity. This may be attributable to that the surface of single ice crystals used were rough on a molecular level.

References

(3) Fletcher, Phil. Mag.,18, (1968) 1287.

COMMENTS

V.F. PETRENKO

1) Using an intensity of this diffusion line can you estimate the thickness of the "liquid-like" layer?
2) When you say "liquid" do you mean just "disordered"?

Answer:

1) Although it is possible to estimate the thickness of liquid-like layer in principle, it is very difficult because the precision of optical system is not so good, and because the intensity of crystalline peak is very strong compared with that of halo diffraction.
2) Yes.

N. FUKUTA

For this kind of experiment, purity of the crystal surface is very important. How did you prepare your sample surface?

Answer:

Ice single crystals were grown by the method of Oguro and Higashi. Polycrystalline samples were grown naturally in a cold room using double distilled water. Both surfaces were mechanically smoothened by microtome.

B. HALE

Can you estimate the minimum thickness of the QLL which it is possible for your apparatus to detect? (I do not mean what is the smallest thickness you observed - but rather what is the resolution of the apparatus)
Answer:

In principle, it is possible by analysing the intensity of crystalline peaks, however, it is very difficult because the decrease of the intensity was widely scattered.