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## ULTRASONIC ATTENUATION IN ICE CRYSTALS NEAR THE MELTING TEMPERATURE

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**Abstract.**- Ultrasonic attenuation in crystals of ice Ih has been measured as functions of frequency (15 ~ 85 MHz) and temperature ( $-8^{\circ}\text{C}$  ~  $-0.1^{\circ}\text{C}$ ). Data were analyzed on the basis of vibrating string model of dislocation, and the following results have been obtained: Density of dislocations is on the order of  $10^6\text{ cm}^{-2}$ ; pinning of dislocations may be due to impurity ions; dislocation density severely fluctuates with time near the melting point.

1. **Introduction.**- The purpose of the present investigation is twofold: to study the origin of the mechanical vibrational loss at high frequencies in ice crystals and to study the dynamical properties of crystals near to the melting temperature. Ice is one of the most interesting materials in regard to its structure and physical and chemical properties (1). About the dynamical properties of ice, internal friction of the crystal at low frequencies (2) and medium frequencies (1) has been studied by many investigators with reasonable success. However, still controversial are the studies at higher frequencies (3 ~ 5). On the other hand, the phenomenon of melting of crystalline solids seems to be still not well understood in spite of many theoretical propositions. One can study the dynamical aspect of the melting transformation by using the acoustic method. Ice is convenient to be used for such a purpose since the experiment is rather easily arranged due to the low melting temperature of the material.

2. **Experimental method.**- Ultrasonic attenuation at sound frequencies of 15 ~ 85 MHz has been measured by the pulse reflection method. The electronic apparatus used are an ultrasonic generator and receiver (Matec model 6000 + 760) and an exponential generator (Matec model 1204A). The sample cell for growing ice crystal by the Bridgman method and for measuring the attenuation in the crystal is as shown in Fig. 1. The main body is a fused-quartz optical cell (A). Boiled commercial pure water filled in the cell is frozen in a refrigerator and then is remelted with leaving a small seed crystal at the bottom of B. Ice crystal is grown from the seed upward through the contracted part C with a

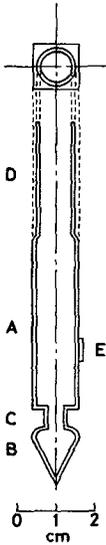


Fig. 1 : Sample cell.

growth rate of about 1.4 mm/h. A gold-plated X-cut 5 MHz quartz transducer 1/4 inch in diameter (E) is bonded to the outer wall of the cell with phenyl salicylate. Temperature of the specimen crystal is measured by a chromel-alumel thermocouple of 0.3 mm in diameter attached to the inner wall of the cell. In usual ice crystals of good quality, number of observable ultrasonic pulse echoes is  $30 \sim 5$  for sound frequencies  $15 \sim 85$  MHz. The accuracy of the attenuation measurement is  $0.005 \sim 0.01$  dB/ $\mu$ sec. The sound velocity in the crystal is determined from the pulse-echo intervals by using a calibrated delayed time marker. The velocity value can be used to determine the crystallographic orientation of the specimen (6).

Possible sources of error in the attenuation measurement will be considered in the following (7). The apparent attenuation caused from the diffraction loss is calculated as  $\alpha_d = 1.7(c/a^2f)$  [dB/cm], where  $c$  is the sound velocity in cm/sec,  $f$  is the sound frequency in Hz, and  $a$  is the radius of ultrasonic transducer in cm. The values converted into decrement  $\Delta (= \alpha c/f$ ; where  $\alpha$  is the attenuation in Np/cm) are on the order of  $10^{-3}$  and  $10^{-5}$  at 15 and 85 MHz. The effect is fairly large at lower frequencies. Effect of nonparallelism of the transducer and the reflector (the opposite wall of the specimen cell) is very

small. The decrement values are on the order of  $10^{-6}$  and  $10^{-5}$  at 15 and 85 MHz. This is due to the good quality of the specimen cell having the wall parallelism better than  $10 \mu\text{m}/45 \text{ mm}$ .

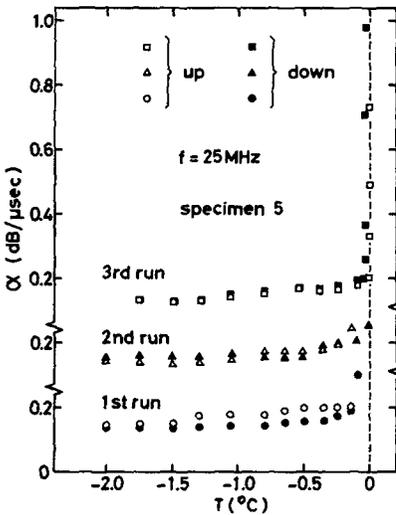


Fig. 2 : Attenuation vs temperature.

3. Results and analysis.- A preliminary study was made on temperature change of ultrasonic attenuation  $\alpha$  in a specimen, and the results are shown in Fig. 2. The attenuation value is stabilized when temperature is raised and lowered repeatedly. This seems to be a kind of annealing effect. It is noted that the attenuation always increases very rapidly at temperatures near to the melting point. These

behaviors are studied more clearly by measuring the attenuation at various sound frequencies. Frequency dependence of decrement  $\Delta$  was determined at various temperatures for a large number of specimens, and examples are shown in Fig. 3. The data points represent the values obtained by subtracting the decrement arising from the diffraction effect from the measured decrement. A broad peak always appears in the  $\Delta$ -vs- $f$  relation, and the peak height increases and the peak position moves toward the lower frequencies as the temperature is raised. The characteristics of the peak are thus not of relaxation type. We anticipate that these peaks are due to the overdamped resonance of vibrating dislocations in crystals (8), and we will proceed to analyze experimental data on this basis.

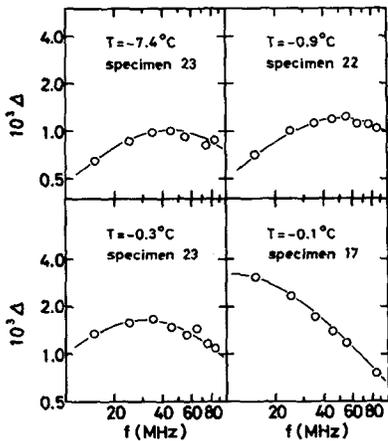


Fig. 3 : Decrement vs Frequency.

For the overdamped resonance, decrement  $\Delta$  can be represented as

$$\Delta = A\omega\tau / (1 + \omega^2\tau^2); \quad (1)$$

$$A = 8n\Omega Gb^2\Lambda L^2 / \pi^3 C, \quad (2)$$

$$\tau = n'BL^2 / \pi^2 C, \quad (3)$$

and here  $\omega$  is the angular frequency of the sound,  $\Lambda$  is the dislocation density,  $L$  is the pinning length,  $B$  is the damping constant,  $\Omega$  is the orientation factor,  $G$  is the shear modulus,  $b$  is the Burgers vector,  $C [= 2Gb^2 / \pi(1 - \nu)]$  is the line tension,  $\nu$  is the Poisson's ratio, and  $n = 4.4$ ,  $n' = 11.9$  for exponential distribution of pinning points. Two parameters  $A$  and  $\tau$

are determined by fitting the above formula (1) to the experimental data. Solid curves in Fig. 3 represent the fitted ones, and the fitting is reasonably good. We further tentatively adopt the expression for the damping constant,

$$B = bE / 10c_t, \quad (4)$$

given by Leibfried (9) derived from the theory of phonon scattering by moving dislocation. Here  $E$  is the lattice energy and  $c_t$  is the velocity of transverse sound. Calculated value of the damping constant is, for example,  $B = 4.6 \times 10^{-5}$  dyn-sec/cm<sup>2</sup> at 0°C. One can thus determine the pinning length  $L$  and the dislocation density  $\Lambda$  in crystals by using the values of  $A$  and  $\tau$  obtained from the experiment.

Concentration of pinning points on dislocations is calculated by  $C = \sqrt{3} b/L$ . Logarithm of  $C$  is plotted against inverse of temperature  $T$  in Fig. 4. Except the data at temperatures near to the melting point,

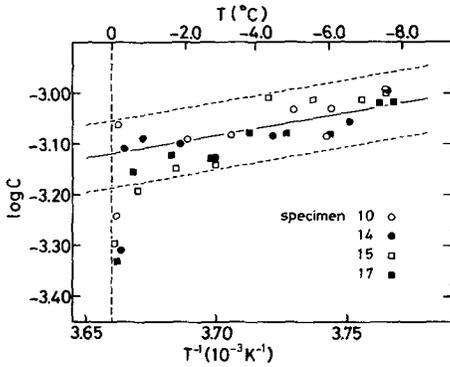


Fig. 4 : Concentration of pinning points vs temperature.

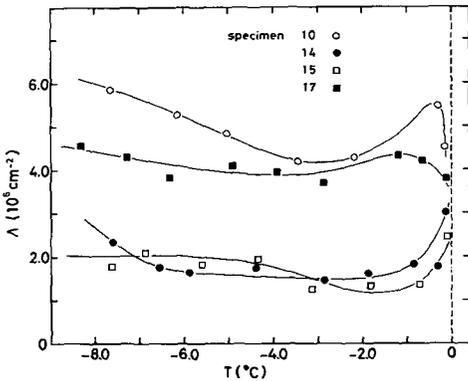


Fig. 5 : Dislocation density vs temperature.

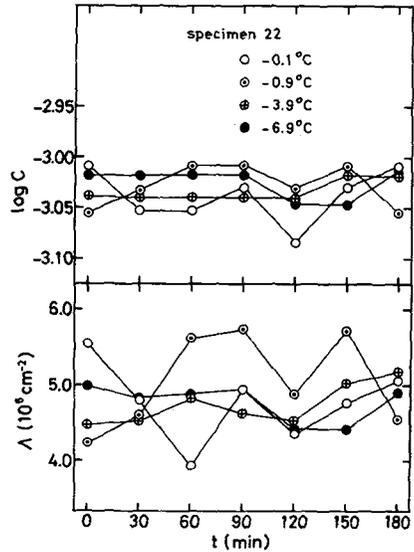


Fig. 6 : Variation of pinning point concentration and dislocation density with time.

C-vs-T relation is well expressed as

$$C = C_0 \exp(U/kT). \tag{5}$$

The obtained values of the constants are:  $C_0$  (concentration of pinning agents in bulk of crystal) = 0.25 ppm, and  $U$  (binding

energy between pinning point and dislocation line) =  $(0.19 \pm 0.03)$  eV. Change of dislocation density  $\Lambda$  with temperature  $T$  is shown in Fig. 5. The value of  $\Lambda$  gradually decreases with increasing  $T$  at lower temperatures, indicating an annealing effect. The behavior of  $\Lambda$  at temperatures near the melting point seems to be not reproducible. Then, we measured the variations of  $L$  and  $\Lambda$  with time as the temperature is held constant, and the results are as shown in Fig. 6. It is clearly seen that both quantities, and especially the dislocation density, are severely fluctuating when temperature is raised near the melting point.

4. Discussion.- In regard to mechanical vibrational loss in crystals of ice, frequency spectrum of decrement is to be as Fig. 7. A large relaxation peak was found at lower frequencies (10), which was attributed to the energy loss arising from reorientation of water molecules (11). As common crystals, a thermoelastic damping peak (7) should appear at

higher frequencies. The peak observed in the present experiment is just between these two peaks above their lower slopes. We considered this peak as due to dislocation damping and analyzed the experimental data. Some discussions will be made on the results of the analysis.

Density of dislocations  $\Lambda$  in our crystals was estimated to be on the order of  $10^6 \text{ cm}^{-2}$ . We have paid not much care to grow crystals of high perfection and the growth rate was rather large. It was found that  $\Lambda$  in artificial ice crystals was proportional to growth rate (12), and  $\Lambda \approx 10^5 \text{ cm}^{-2}$  in Czochralski-grown crystals at the same growth rate as ours. Generally speaking,  $\Lambda$  in crystal grown by the usual Bridgman method is even higher because of the effect of walls of container. We have used specimen cell of square shape, which is not so good if the purpose of experiment is to grow low- $\Lambda$  crystals. Thus the above value of  $\Lambda$  in our ice crystals seems to be not so unreasonable.

Dislocations were shown to be pinned by some pinning agents with concentration of 0.25 ppm in crystals. This value is larger than the concentration of intrinsic point defects in ice, namely, ionic defects and orientational defects (1). Ion chromatographic analysis of the ice crystals used in our experiments has been made, and detected impurity ions were  $\text{F}^-$ ; 0.04 ppm,  $\text{Cl}^-$ ; 0.29 ppm,  $\text{SO}_4^{--}$ ; 0.06 ppm. We imagine that  $\text{Cl}^-$  ions are the main pinning agencies in the present case. Calculated elastic interaction energy of Cl atom and dislocation line is, however, only about 0.08 eV. It is very possible that interactions other than elastic one mainly contribute to the binding between the two defects.

In the analysis of our experiments, we assumed that the vibration of a dislocation line was damped by an elementary process against the motion, namely, the impingement of phonons on dislocation, and we used the value of damping constant  $B \approx 10^{-5} \text{ dyn}\cdot\text{sec}/\text{cm}^2$ . On the other hand, X-ray topographic studies of individual dislocation motion (13, 14) showed that  $B \approx 10^3 \text{ dyn}\cdot\text{sec}/\text{cm}^2$ . If this value is used in our analysis, calculated dislocation density becomes extremely large. We consider that the mechanisms of the damping of dislocation motion are different in the two cases. In large-scale motion of dislocation in ice crystal, there may be reorientation and recombination of the broken O-O bonds and redistribution of protons around them. These processes should produce large forces against the dislocation motion. In the present

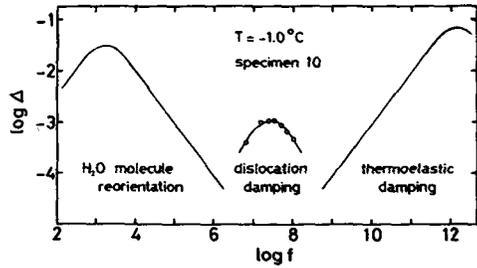


Fig. 7 : Frequency spectrum of decrement.

case of ultrasonic experiment, however, the displacement of dislocation loop is as small as a lattice parameter or less. Under such condition, the above damping mechanism is not likely to be effective.

Near the melting temperature, ultrasonic attenuation increases rapidly, which is interpreted as mainly due to increase of density of dislocations. This increase of dislocation density and also its fluctuation with time are both tentatively considered to be connected with an idea of spontaneous generation of dislocations in melting crystals (15).

Finally, it must be said that there are models of dislocation damping other than the vibrating string model we adopted. Kink model can be adaptable at lower temperatures for materials with high Peierls stresses (16). Non-crystalline dislocation core model was also proposed in dealing with the damping of dislocations in ice crystals (17). We do not say at present which is truly most convenient for ice crystals, and we regard our present report as a preliminary and not the final one.

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