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# Internal Friction of Ice. II

## The Grain Boundary Internal Friction of Ice\*

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### Abstract

The grain boundary internal friction of polycrystalline ice grown from a melt was measured by analyzing the individual crystal boundaries. The grain boundary internal friction was not always proportional to the total area of the boundaries, but depended upon the chemical impurities concentrated at the boundary zone. Estimated values for the activation energy of grain boundary viscosity were found to be about 60 to 70 kcal/mole for pure H<sub>2</sub>O and D<sub>2</sub>O ice, and those for NaCl-doped ice crystals decreased from 60 to 30 kcal/mole with an increase in the concentration.

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### 1. Introduction

When the internal friction of polycrystalline ice was measured as a function of temperature, it was observed that the internal friction ( $\tan \delta$ ) decreased very rapidly from high values near the melting point to very low values with a decrease in the temperature, and then increased again toward a maximum value due to proton movement. There is no doubt that the steeply rising (or descending) values for  $\tan \delta$  in the temperature range between 0°C and -30°C are caused by the grain boundaries, because this phenomenon has never been observed in single-crystal ice.

In our experiment with NaCl-doped ice crystals, the steep grain boundary curve shifted toward the high temperature range with an increase in frequency, and toward the low temperature range with an increase in NaCl concentration (KUROIWA 1964, Figs. 7 and 13). The dependence of grain boundary internal friction on frequency and impurity concentration implies that the grain boundary

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internal friction in polycrystalline ice could be caused by grain boundary viscosity as found in polycrystalline metals by K&E (1947). It is also known that chemical impurities will concentrate at the grain boundaries rather than inside of individual grains, with the amount of concentration different in each boundary. In contaminated polycrystalline ice, therefore, every grain boundary will have a different value for  $\tan \delta$ . The purpose of this paper is to determine what mechanism is responsible for grain boundary internal friction. This investigation indicates that the grain boundary internal friction of polycrystalline ice is not always proportional to the total area of the crystal boundaries involved and that concentrated chemical impurities play an important role in grain boundary viscosity.

## II. Internal Friction of Welded Boundaries

The resultant internal friction curves of two combined crystals composed of pure and contaminated single crystal ice have been illustrated and discussed in previous paper (KUROIWA 1964, Fig.21). This experiment was conducted originally for the sake of interpretation of a bimodal relaxation curve which appeared in  $\text{NH}_4\text{F}$ -doped ice crystals, but it also provides a useful technique in the measurement of internal friction at individual grain boundaries.

In this former experiment, two combined crystals were made by welding the two separate specimens together at the melting point. One had a narrow welded interface and the other a broad interface. Since the crystallographic orientation was quite different in both crystals the welded interface can be considered to be an artificial grain boundary. The total interface areas of these two combined crystals are estimated from their dimensions to be  $38.8 \text{ mm}^2$  for the narrow interface A and  $2510 \text{ mm}^2$  for the broad interface B. If we recognize that a grain boundary should have internal friction in the high temperature ranges between  $0^\circ\text{C}$  and  $-30^\circ\text{C}$ , a steep variation of  $\tan \delta$  should be observed at the artificial grain boundaries in the combined crystals. Contrary to this assumption, the experimental data showed that the welded area produced no internal friction. However, a small rise of the resultant internal friction, shown by a thick arrow in Fig. 21 (KUROIWA, 1964), can be attributed to the contaminated crystal. If this small rise of  $\tan \delta$  had originated at the welded boundary, a high value for it should have been observed in specimen B, because the total welded area of B is about 65 times larger than that of A.

It is interesting to note that the welded boundary between two crystals does not produce any internal friction in the frequency ranges used. (A reasonable explanation will be given later.) These experimental results can be useful

in determining the internal friction of individual grain boundaries in polycrystalline ice.

### III. Internal Friction at Individual Crystal Boundaries

A square ice plate (2 cm  $\times$  2 cm) containing a Y-shaped grain boundary was cut from a block of commercial ice. Two rectangular single-crystal ice bars were welded to each side of this square ice plate. Then it was trimmed by a microtome to the dimensions 185 mm long, 15 mm wide, and 2.7 mm thick. Figure 1 shows this "inlaid" grain boundary photographed under crossed polaroids; a-b and c-d are welded boundaries between the square ice plate and single-crystal plates, and p-q-r-s are Y-shaped crystal boundaries. In order to show relative crystallographic orientations of both crystal and welded boundaries, evaporation etch pits were produced by a Formvor film application developed by HIGUCHI (1958). In Fig. 1, picture A and B represent the etch pits produced at the crystal boundaries p-s and r-s, C and D are the etch pits at the welded interfaces a-b and c-d, respectively. This specimen was placed in a cold box and the internal friction was measured by the flexural vibration method as described in previous paper. The fundamental frequency of this specimen was 240 c.p.s. In Fig. 2, curve (A) depicts the internal friction of the inlaid Y-shaped crystal boundaries (A)'. A steep rise in  $\tan \delta$  is seen near the melting point. This can be attributed to the Y-shaped crystal boundaries only, because the internal friction could not have been produced at the welded interfaces.

Another linear grain boundary was cut from the same block of commercial ice and inserted between two single crystal ice bars in the same manner as before, (see (B)' in Fig. 2). The specimen was trimmed so that it would have approximately the same frequency as specimen (A)'. The grain boundary internal friction of this specimen is illustrated by curve (B) in Fig. 2, showing a greater damping than that of the Y-shaped boundaries. A new grain boundary was inlaid in the same specimen as shown in Fig. 2 (C)'. Curve (C) shows the subsequent increase of  $\tan \delta$  due to the additional crystal boundary.

Curve (D) in Fig. 2 represents the steep rise of  $\tan \delta$  for an ice bar cut from ordinary commercial ice composed of many small grains (D)'. The average grain size was 7 mm to 10 mm. No remarkable difference is observed between (C) and (D), though the total area of crystal boundaries of (D)' is very much greater than that of (C)'. Hence it appears that grain boundary internal friction in contaminated polycrystalline ice is not always proportional to the total area of crystal boundaries, but depends upon concentrated chemical impurities. The concentration of chemical impurities may differ from boundary

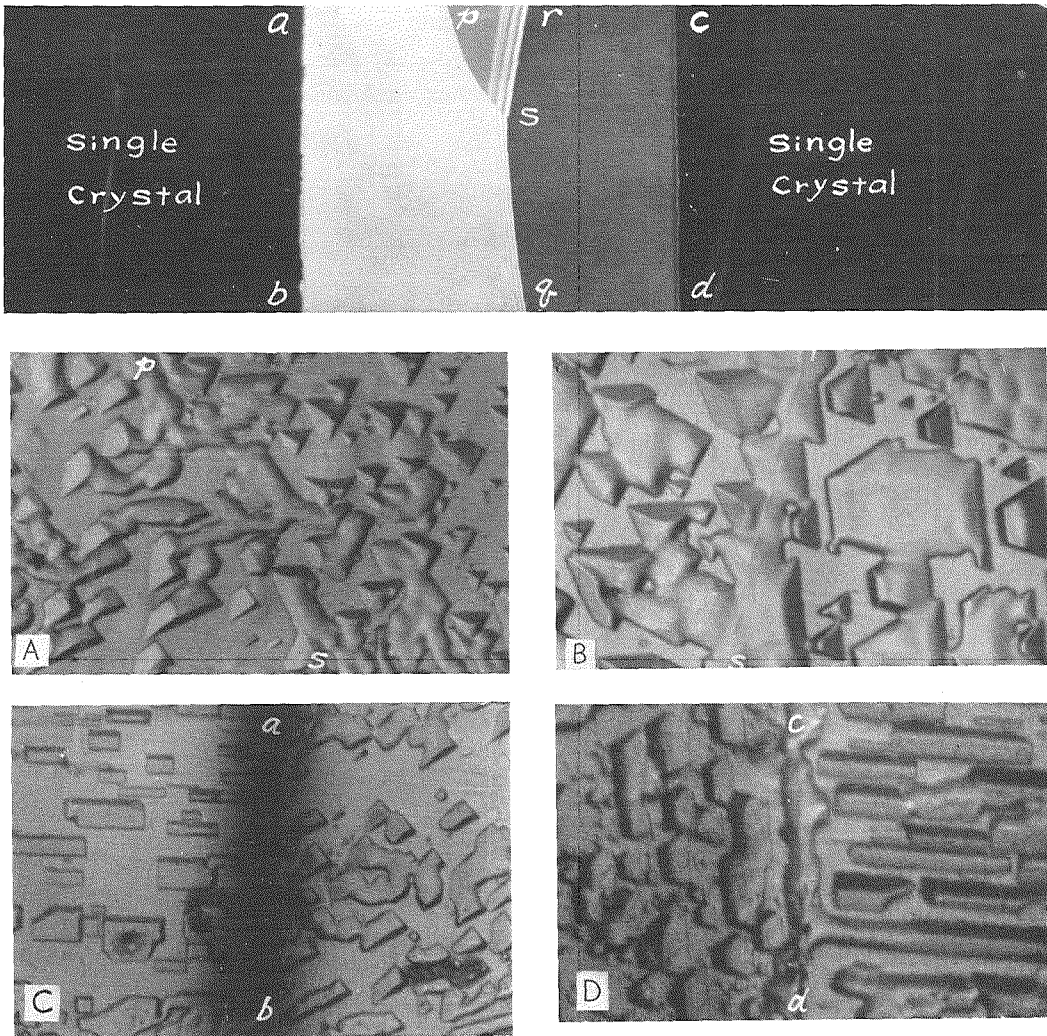


Fig. 1. Inlaid Y-shaped grain boundaries. a-b and c-d are welded boundaries. A and B are etch pits produced along natural grain boundaries. C and D are etch pits produced along welded boundaries

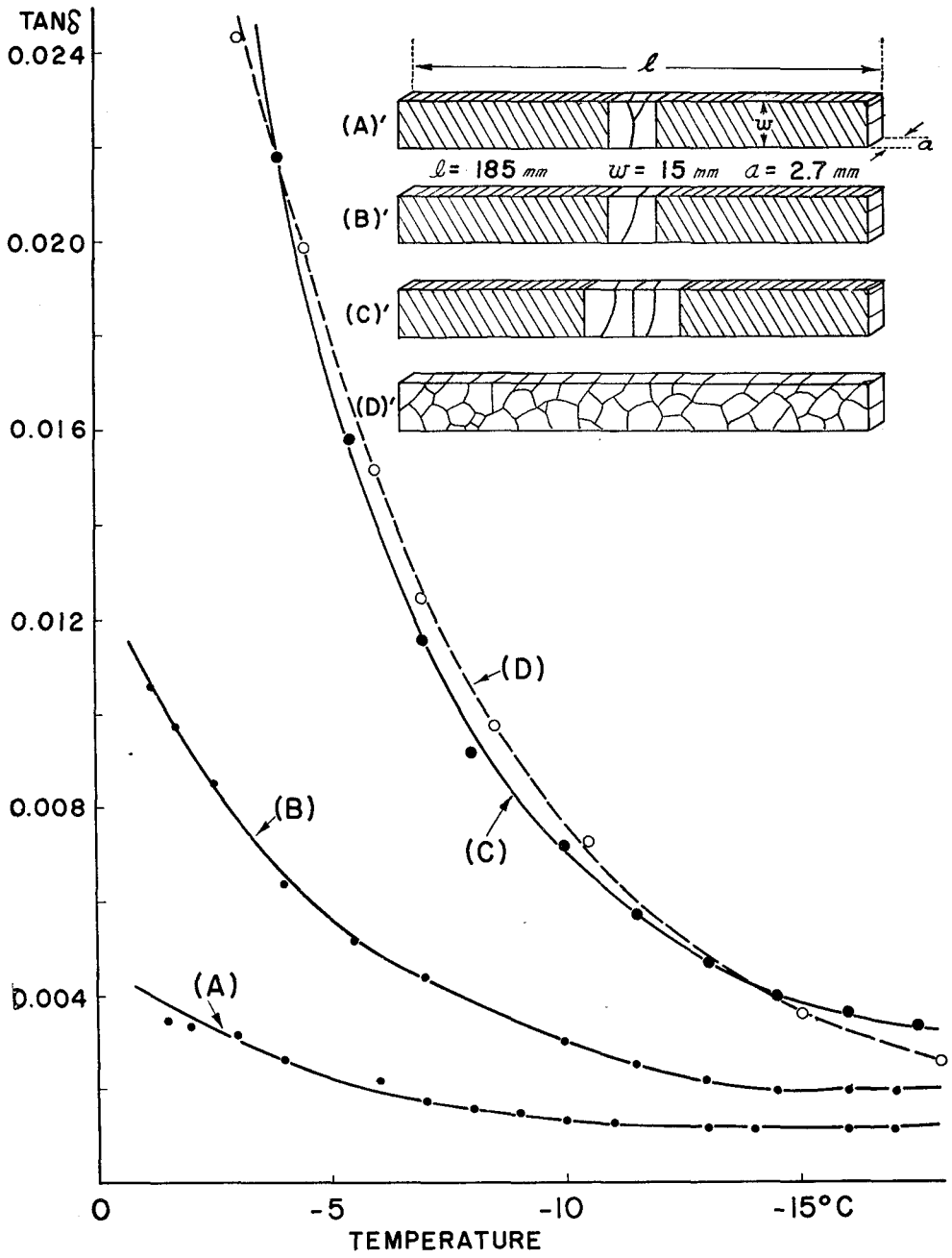


Fig. 2

to boundary.

Further confirmation of this inference was obtained by the following experiment. Two distinctly different crystal boundaries were obtained, one from a pure ice specimen and the other from an NaCl-doped ice crystal grown from a 0.001 mole solution. The ice block containing the grain boundaries from the pure ice sample was inlaid and welded between two single-crystal ice bars,

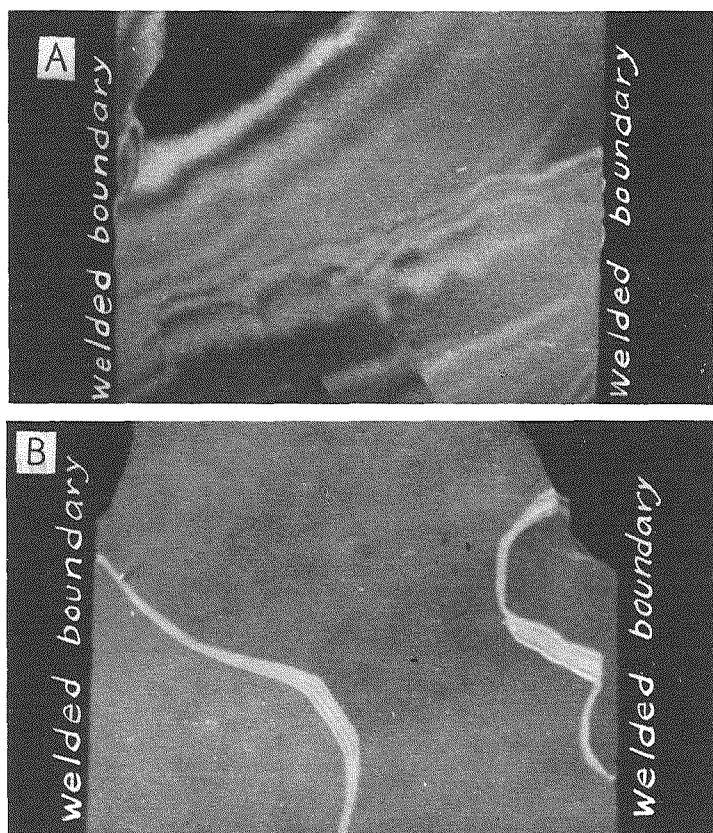
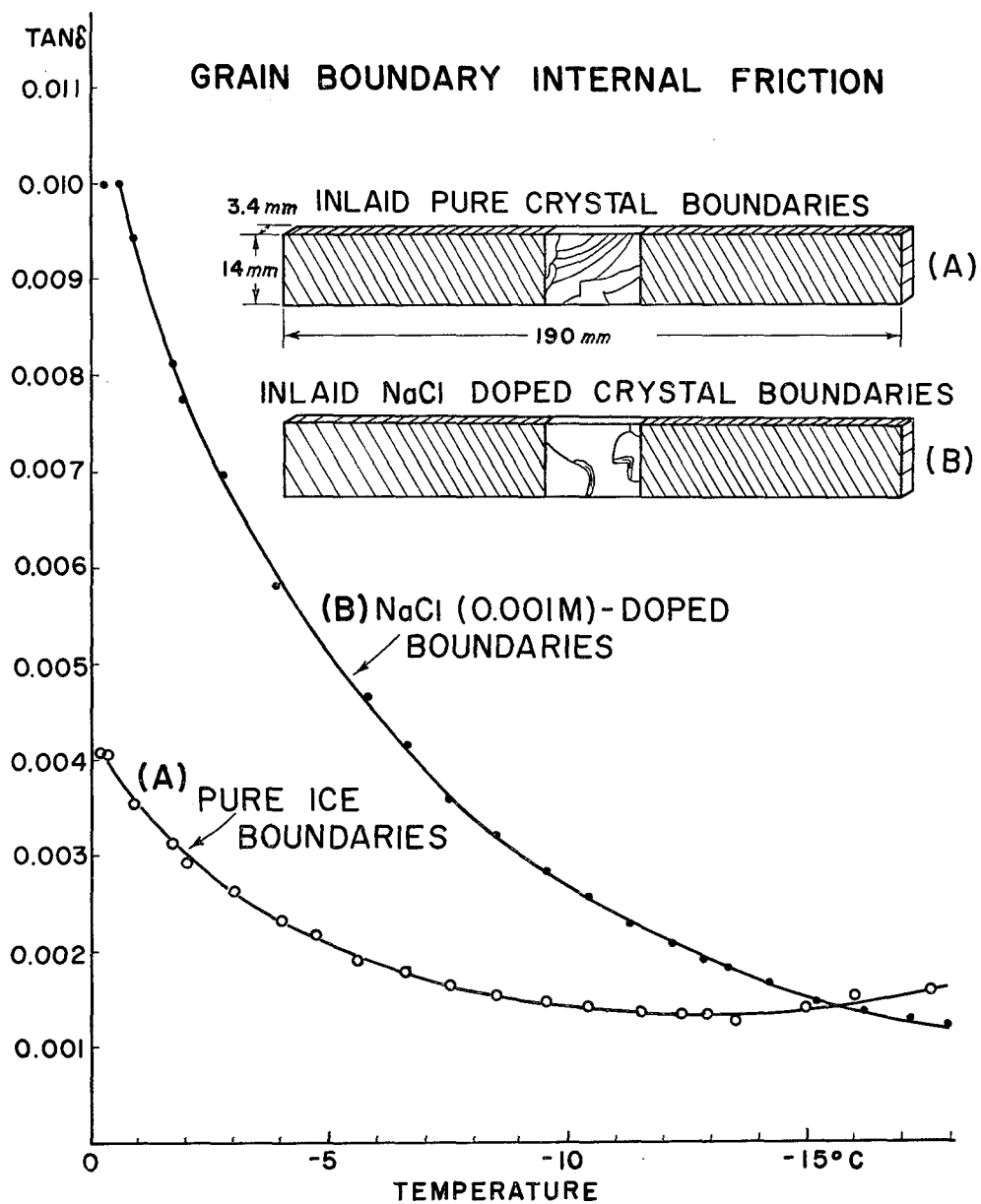


Fig. 3. Structure of inlaid grain boundaries of pure ice A and NaCl-doped ice B

and the same procedure was repeated for the doped block. The bars were then trimmed to the same dimensions, so that they would produce equal frequencies. In Fig. 3, photographs A and B show the structure of the inlaid crystal boundaries of both specimens taken under crossed polaroids. The structure of the pure ice crystal boundaries is much more complicated than that of the NaCl-doped ice crystal boundaries.



**Fig. 4.** Comparison of the internal friction of inlaid crystal boundaries in pure ice (A) and NaCl-doped ice (B)

In Fig. 4, curves (A) and (B) represent the grain boundary internal friction of both specimens measured at the fundamental vibration (305 c.p.s.). Inspection of the data shows clearly that the crystal boundaries containing NaCl have a higher internal friction than boundaries free of chemical impurity. This experiment clarifies the influence of chemical impurities on mechanical damping at crystal boundaries.

According to K $\hat{E}$ , grain boundary internal friction in polycrystalline metals is produced by "grain boundary viscosity". It is reasonable to expect that a concentration of chemical impurities would cause lowering of the freezing temperature, producing a thin liquid-like film at crystal boundaries. Therefore, it can be considered that the steep rise of  $\tan \delta$  near the melting point in polycrystalline ice is caused by a viscous layer at grain boundaries. As mentioned before, the artificially welded grain boundary interface of two crystals shows no appreciable internal friction. This fact is quite natural for when two crystals were welded together at the melting point, melted water was squeezed out of the welded interface by compression, leaving no chemical impurities.

#### IV. Activation Energy for Grain Boundary Viscosity

If we assume that the grain boundary internal friction in an ice crystal is caused by anelasticity due to grain boundary viscosity, a steeply rising curve near the melting point should exhibit a well defined maximum. The location of the maximum should move toward the high temperature range with an increase of frequency, and the dispersion of resonant frequency should also occur in the same temperature range. In our experiment, however, no maximum damping was observed, though the steep rise of  $\tan \delta$  appeared showing a temperature shift with frequency. The main reason why it was impossible to observe maximum damping was the high frequency used. The observed steep curves of  $\tan \delta$ , therefore, can be considered to be slopes coming down from "hidden maxima". In order to observe the complete shape of maximum damping of the grain boundary internal friction, the measuring frequency must be lowered as much as possible.

If the following approximation is permitted, we can estimate roughly the activation energy for grain boundary viscosity. Fig. 5 (A) depicts grain boundary internal friction observed in NaCl-doped ice crystallized in a 0.001 mole solution. The curves show parallel displacement toward the high temperature range with increasing frequency. A horizontal line cutting all of the slopes at a point where they are parallel, provides a means of determining the absolute temperature difference between any two slopes. This temperature difference

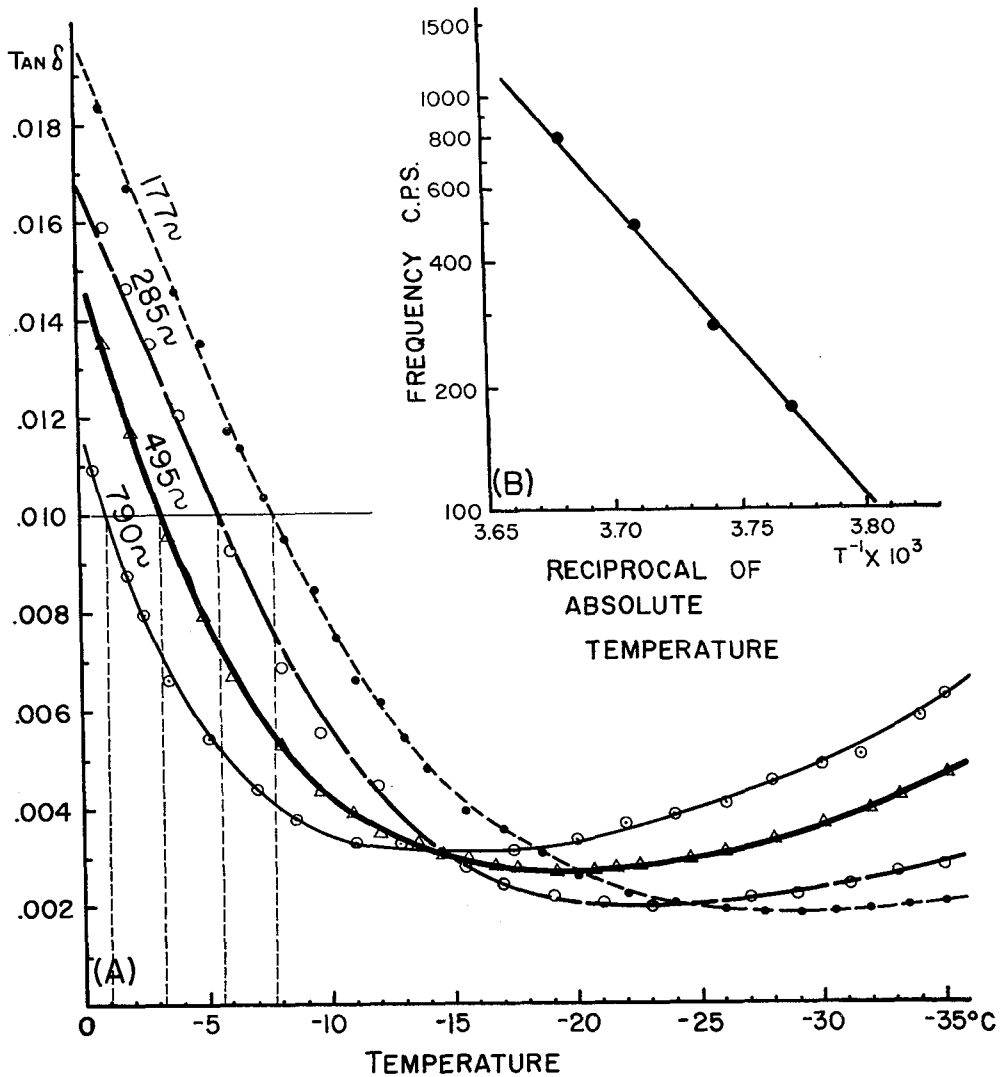


Fig. 5. Grain boundary internal friction in NaCl-doped ice

is then assumed to be the same as the temperature between the maximum of the corresponding slopes. A horizontal line is drawn at  $\tan \delta = 0.010$ , at which level it cuts the four curves at  $-7.8^\circ\text{C}$ ,  $-5.6^\circ\text{C}$ ,  $-3.2^\circ\text{C}$  and  $-1.0^\circ\text{C}$ , respectively. A linear relationship exists between the reciprocal of absolute temperatures and their related frequencies (Fig. 5 B). The resulting activation energy equals approximately 30.9 kcal/mole.

The same procedures were applied to many specimens of pure and doped ice crystals in order to obtain the activation energy for grain boundary viscosity.

The results are:

pure H <sub>2</sub> O-ice	74.5 kcal/mole	NaCl-doped ice	
	57.5 " "	0.005 mole	30.9 kcal/mole
D <sub>2</sub> O-ice	55.9 kcal/mole	0.001 "	30.6 kcal/mole
	57.5 " "	0.0005 "	42.0 kcal/mole
		0.00005 "	51.6 kcal/mole
		0.00001 "	59.2 kcal/mole
HCl-doped ice			
	0.002 mole	36.0 kcal/mole	
Commercial ice		32.0 kcal/mole	(average of 5 samples)
HF-doped ice			
	0.0025 mole	59.0 kcal/mole	

Inspection of these data shows that the activation energy for grain boundary viscosity of pure H<sub>2</sub>O and D<sub>2</sub>O ice is approximately two times higher than that of NaCl-, HCl-doped ice crystals, or commercial ice. In NaCl-doped ice crystals, the activation energy decreased with an increase in concentration. The activation energy for HF-doped ice was the same as the value for pure ice. Since these data were obtained through a procedure which is based on an assumption, the data may deserve reexamination in future studies concerning this problem.

#### V. Concluding Remarks

The grain boundary internal friction was measured by cutting blocks containing individual crystal boundaries from polycrystalline ice and inlaying these in single crystal bars. It was confirmed that grain boundary internal friction differs from boundary to boundary, and that it is not always proportional to the total area of the boundaries but depends upon concentrated chemical impurities.

The activation energy for grain boundary viscosity was estimated assuming that the shift of observed curves of  $\tan \delta$  toward the high temperature range with increasing frequency is due to anelasticity at grain boundaries. The estimated values for activation energy were roughly 60 kcal/mole for pure ice and 30 kcal/mole for doped ice.

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