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Preface

The internal structure of a solid has an important influence on how the solid will deform under an applied load. A very useful technique for obtaining information on internal structures is to determine, as a function of temperature and frequency of stressing, the rate at which internal strain energy is dissipated within the solid. Scientists at the Institute of Low Temperature Science at Hokkaido University, Sapporo, Japan, have used this technique with great success in their investigations on ice and snow. The results of their observations should be given serious attention in any study on the deformation behaviour of these materials.

The present paper, translated from the Japanese at the request of the Snow and Ice Section of the Division of Building Research, National Research Council, presents some of the recent observations made at the Institute of Low Temperature Science on the internal friction of polycrystalline and single-crystal ice. It is the second paper on this subject by this group that has been translated, the first being available in the translation series of the Defence Research Board (Visco Elasticity of Ice in the Temperature Range 0° - 100°C , by K. Yamaji and D. Kuroiwa, Defence Research Board T63J, August 1958).

The Division of Building Research wishes to express its appreciation to Mr. E.R. Hope of the Defence Research Board for the excellent translation of this paper.

Ottawa,
September 1961.

R.F. Legget,
Director.

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INTERNAL FRICTION OF POLYCRYSTALLINE AND SINGLE-CRYSTAL ICE

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Received July, 1959.

Author's Résumé

The internal friction of polycrystalline and single-crystal ice was measured by a flexure vibration method in the temperature range 0°C to -180°C. For cooling the specimen, use was made of a cold box which could be refrigerated by means of liquid nitrogen or oxygen. The experimental apparatus is shown in Figure 1.

In the case of polycrystalline ice the internal friction, here designated by $\tan \delta$, revealed three characteristic variations within the above-mentioned temperature range (see Fig. 4). Within the range of 0° to -30°C $\tan \delta$ was found to decrease exponentially, and, as the temperature was further lowered, there appeared two peaks of $\tan \delta$. The position of the maximum of $\tan \delta$ which appeared in the intermediate temperature range proved to depend on the vibration frequency in such a way that it shifted towards the higher temperature side as the frequency was increased, while the position of the other peak located in the vicinity of -145°C was independent of the frequency. In contrast to polycrystalline ice, single-crystal ice did not show anything like an exponential decrease in $\tan \delta$ in the range 0° to -30°C; it exhibited a $\tan \delta$ peak which shifted with increasing frequency towards the higher-temperature side (see Figs. 5, 6).

We also made some experiments to investigate whether $\tan \delta$ of ice is affected or not by internal strains produced after irradiation with heat rays. It was found that the peak of $\tan \delta$ which appeared in the intermediate temperature range, in either polycrystalline or single-crystal ice, was not influenced by the internal strains due to Tyndall's figures, minute cracks or the like, resulting from irradiation (see Figs. 7, 8). $\tan \delta$ of polycrystalline ice in the range 0°C to -30°C, on the contrary, was considerably affected by thermal radiation (see Fig. 9). Two different activation energies were calculated, one from the curve of $\log \tan \delta$ versus reciprocal absolute temperature and the other from the shift of $\tan \delta$ observed in the intermediate temperature range (see Figs. 10-13). The former value came out to about 16-20 Kcal/mol, and the latter to 6 Kcal/mol.

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I. Introduction

When a solid rod is set freely vibrating, the amplitude of the oscillations will decay with the passage of time. The rate of decrement is more rapid, the greater the internal friction of the solid. The internal friction of solids, a very sensitive index of structure, has long been used as a powerful method for analysing the internal structure of metals, in connection with the imperfections of crystals, such as lattice defects, dislocations, atomic impurities and so forth.

Ice is a substance that markedly differs in its physical properties from metals and other solids, and concerning its internal structure there are many things we do not know. Measurements of the internal friction of ice over wide ranges of temperatures would seem to be one effective means of investigating its internal structure. As our experimental material for the internal friction measurements we used ordinary commercial ice, single-crystal ice prepared in the laboratory, and glacier ice from Greenland, brought back to Japan by Professor Nakaya. The glacier ice is quite different genetically from the other two types, being formed by recrystallization and sintering of

particles under enormous pressures acting over a long period of time. How these differences of structure and origin manifest themselves in the internal friction is a question of great interest.

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II. Experimental Arrangement

The internal friction of ice was measured by a flexure vibration method. * The said friction is in general a function of the vibratory frequency and of temperature. In order to extend the temperature range of the measurements as much as possible, the experimental apparatus was placed in a cold-box which could be refrigerated with liquid oxygen or liquid nitrogen.

Figure 1 shows the general layout of the apparatus. P_1 and P_2 are thin bars of ice, of rectangular cross-section, cut out of the same ice-block and trimmed to exactly the same dimensions. P_1 was used for temperature determinations, and P_2 for the internal friction measurements. To each end of P_2 thin iron plates are affixed. (Alternatively, these plates may be frozen on. It is, however, preferable to avoid doing this, because when the temperature is lowered to that of liquid oxygen, cracks due to the different coefficients of thermal expansion may appear in the test-pieces.) Immediately below the iron plates and at a distance of about 5 mm there are two electromagnets C_1 and C_2 . P_1 and P_2 are each supported in a level position, at their oscillatory nodes, by two fine silk threads stretched between the two metal U-brackets B. The brackets B and the magnets C_1 and C_2 are mounted on a sturdy metal base. Their positions are freely alterable to suit the dimensions of the experiment. The whole apparatus, in advance of the experiment, is set up in the cold room, and enclosed in the cold-box L which is refrigerated by circulating liquid oxygen or nitrogen. The outside of the box is packed with styrofoam, a good thermal insulator.

The ideal procedure would be to measure the specimen temperature by a thermocouple directly in contact with P_2 , but since this would affect the damping of the vibrations, we decided to take as equivalent to the temperature of P_2 the temperature measured by a thermocouple in contact with the ice-bar P_1 , which is shaped to the same dimensions and located in a position where the thermal conditions are about the same as for P_2 . Since a mobile regulation of the temperature in this apparatus would be difficult, our procedure was to prolong the circulation of liquid oxygen or nitrogen, cooling the system until the temperature of P_1 stood equal to the boiling point of the refrigerant; then the supply was shut off and the measurements were conducted during the subsequent free rise of the temperature. The rate of rise was satisfactorily slow; it took about eight hours for the temperature in this apparatus to come up from that of liquid oxygen to -3°C . The cold-box was made in three sizes, $45 \times 18 \times 12 \text{ cm}^3$, $24 \times 13 \times 12 \text{ cm}^3$, and $15 \times 13 \times 12 \text{ cm}^3$, to suit the size of the test-pieces.

If alternating current is supplied to the magnet coil C_1 and its frequency continuously varied, P_2 will begin to vibrate, and at resonance, when

* For details of the method see references 1, 2, 3 and 4.

the impressed frequency matches the natural vibratory frequency of P_2 , the induced current in coil C_2 will reach its maximum. At this point we short-circuit the current in C_1 , leaving P_2 in free oscillation, with a gradually decaying amplitude. If f is the natural vibratory frequency of P_2 and t_1/n is the measured time required for the amplitude to fall to $1/n^{\text{th}}$ of its original value, then Young's modulus E and the quantity $\tan \delta$, proportional to the internal friction, are given by the formulae

$$E = \frac{48\pi^2 \ell^4 \rho}{m^4 a^2} f^2 \quad (1)$$

$$\tan \delta = \frac{\log_e n}{\pi \cdot f \cdot t_1/n} \quad (2)$$

Here m is a constant determined by the mode of vibration, ℓ is the length of specimen P_2 , a is its thickness, and ρ is the density.

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III. Experimental Results

In Figure 2 we show photographs, in polarized light, of representative specimens of the kinds of ice used in the experiments. (A) and (B) are commercial ice of polycrystalline structure. (A) is cut from a large block of ice, with the face normal to the direction of freezing; in (B) the face is parallel to the direction of freezing. (A) is 17 cm in length, so that the crystal grains in the photograph are 10 mm to 5 mm in size. (C) and (D) are artificial single-crystal ice prepared in the laboratory. In (C), however, there was a sudden change of conditions midway in the freezing process, with the result that the sample came out divided into two single crystals, with a discontinuity in the orientation. That is to say, there are two single crystals joined together at a single grain boundary. (D) is a perfect single crystal, showing no grain boundary structure. What is meant here by "perfect" is that no matter how the polarizer is rotated no distortion whatever can be detected in the interior of the crystal. After completion of the experiments, ethylene dichloride solution of formvar (used for replicas) was applied to the single-crystal ice, producing pits, and from the direction of the crystal surfaces as revealed by the pits the orientation was determined. The crystal axes were determined by Higuchi's method.

When we measure the internal friction of a solid by the vibration method, this quantity is not a function of temperature and vibration frequency alone, but will also, depending on the causes that produce the internal friction, vary greatly with the amplitude of the vibrations. Since in the case of our experiments the specimens were enclosed in the tightly sealed cold-box of Figure 1, the vibratory amplitude could not easily be determined. Therefore with ice the necessity arises of investigating in advance how much the internal friction alters with the vibratory amplitude. Figure 3 shows the changes of internal friction occurring in ice-bars of the dimensions shown when, in the cold room, they were caused to vibrate with an amplitude that was varied from 10 μ to 800 μ . The vibratory amplitude is

plotted as abscissa, in microns. The ice-specimens used in the experiments were of commercial polycrystalline ice and, as shown schematically in the Figure, were cut with their [broad] faces perpendicular to and parallel to the direction of freezing. The vibratory amplitudes were determined by observing, with a horizontal microscope, the deflections of a small boss on the surface of the ice, illuminated obliquely by a strong light. The boss, shining in the field of the microscope, could be observed when the bar was set vibrating. (Cf. Teion Kagaku, 15, p.44.) Figure 3 shows that although the amplitude of the vibrations changes greatly, the quantity $\tan \delta$ does not appear to alter very markedly. In our subsequent measurements, all vibratory amplitudes were kept as small as possible --- within limits of a few microns.

i) The internal friction of polycrystalline ice. Figure 4 shows our experimental results on polycrystalline commercial ice. Curves (1-5) are a series of measurements at varying vibration-frequency made on test pieces cut with their faces normal to the direction of freezing, while curve (6) is for a specimen cut parallel to the direction of freezing. In curve (1), a bar of length 38.7 cm, width 19.3 cm and thickness 0.7 cm is measured at its fundamental frequency. The readings were begun at the low-temperature end. As the temperature rises, $\tan \delta$ exhibits, at -145°C , a peak of height 0.005. With further rise of temperature $\tan \delta$ decreases, only to exhibit, at -75°C , its sharp maximum peak of height 0.01. Again $\tan \delta$ diminishes as the temperature rises, and in the neighborhood of -30°C reaches a minimum; then as the temperature approaches the melting point $\tan \delta$ increases exponentially. Curve (2) is measured on the same specimen at the first harmonic overtone, corresponding to about 2.73 times the fundamental frequency of vibration. In this case, the supporting points of the ice-bar were transferred from the nodal point of the fundamental vibration to that of first harmonic overtone. The whole picture remains about the same: two peaks appear in $\tan \delta$, and there is a rapid rise as the melting point is approached. But there are also differences from curve (1). The low-temperature $\tan \delta$ peak in the vicinity of -145°C is tending to decrease, while the temperature at which the peak in the middle range appears has been displaced to the high side (-63°C) as compared with the fundamental-frequency curve. Now let us turn to curve (3), which represents the variation of $\tan \delta$ measured at the second overtone, corresponding to about 5.4 times the fundamental frequency. Again we see a diminution of the peak in the low-temperature region and a displacement of the mid-range maximum to a higher temperature. Curve (4) is measured at the fourth overtone, about 13.3 times the fundamental frequency. Here, however, the specimen had been planed down to a thickness of 0.51 cm, because after completion of curve (3) its dimensions had become rather irregular as a result of sublimation. Consequently the fundamental frequency was slightly lower --- about 99.5 cycles --- than the original value, so that the frequency of the fourth overtone, in curve (4), was 1318 cycles. In this curve the low-temperature $\tan \delta$ peak has practically disappeared, while the mid-range peak has shifted to a still higher temperature; the peaks themselves have become considerably lower as compared with their initial heights in curve (1).

At this point in the experiment, the specimens had been subjected to four successive thermal variations over a wide range of temperatures, from near the melting point to the low temperature of liquid oxygen. If there were any hysteresis involved in the thermal characteristics of $\tan \delta$ in ice, then if we moved back to the fundamental frequency and repeated the measurements, $\tan \delta$ would not be likely to reproduce its original values. To

investigate this matter we now plotted $\tan \delta$ curve (5) at the fundamental frequency. As we have explained, the test-piece thickness had meanwhile been changed in the truing-up operation, so that the frequency was smaller than in the case of curve (1). The low-temperature peak of $\tan \delta$ was nevertheless still in the same place, but the peak in the middle region, as one would expect with the reduced frequency, appeared at a lower temperature (-70°C) than in curve (1). No noticeable hysteresis effect is seen in the over-all form of the curve nor in the peak values.

Curve (6) represents values of $\tan \delta$ measured at the fundamental frequency of vibration in a polycrystalline specimen of almost the same size, cut with its faces parallel to the direction of freezing. Although the distribution of the crystal grains is markedly different as compared with the former specimen, there is practically no change in the temperature-behavior of $\tan \delta$.

The top part of Figure 4 shows Young's modulus for ice, measured in the same range of temperatures. The numbers on the curves refer to measurements as follows: curve (1), for the fundamental frequency; curve (2), for the first overtone; curve (3), for the second overtone. In the vicinity of -10°C , Young's modulus has a value of 7.2×10^{10} , and increases with decrease of temperature; at -180°C it becomes 8.5×10^{10} .

The temperature characteristics of $\tan \delta$ for polycrystalline ice may be summarized as follows. Over the temperature range from 0°C to -180°C , $\tan \delta$ of polycrystalline ice exhibits three distinctive variations. First, from 0°C to -35°C there is a rapid fall of $\tan \delta$. Second, in the middle range from 35°C to -120°C a large maximum of $\tan \delta$ develops, the peak value of which decreases with increasing vibration frequency, while simultaneously the temperature at which the peak appears is displaced to the high side. Third, there is still another peak in the region around -145°C . In this case the peak values decrease with increasing vibration frequency, but the temperature at which the maximum occurs does not shift with frequency.

Next we shall show how the temperature characteristics of $\tan \delta$ for single-crystal ice differ from those for polycrystalline ice.

ii) The temperature characteristics of single-crystal ice. Figure 5 shows measurements of $\tan \delta$ for an artificial single-crystal ice produced in the cold chamber by freezing ordinary tap water. The single crystals, flaw-free parts of the ice exhibiting no distortion under crossed polaroids, were cut out and shaped into rectangular test-bars. We were able to obtain them quite large, the biggest being 17 cm long, the smallest 13 cm. (The crystals were produced by Mr. Wakahama of our Institute [6].) Curves (1), (2) and (3) respectively represent measurements of $\tan \delta$ at 510, 870 and 2350 cycles, made on single-crystal specimens having the C-axis lengthwise of the rectangular bar; that is, with their slip-planes parallel to the direction of vibration. The order of the measurements was as follows. First we took curve (2) at the fundamental frequency of 870 cycles, then curve (3) at the first harmonic overtone, and finally, after trimming down the thickness of the specimen, curve (1). The values of $\tan \delta$ are plotted as ordinates on a scale magnified five times as compared with the scale of Figure 4. To show how small the internal friction of these crystals is in comparison with that of the polycrystalline ice, we have added curve (5), representing one set of polycrystalline

ice measurements from Figure 4. Branch b of curve (5), after passing through the peak value at 0.008 (not shown in the Figure), connects to branch b'. Since curve (5) is for frequency 842 cycles, the single-crystal values for nearly the same frequency, as seen in curve (2), are indicative of the reduction in the internal friction of single-crystal ice as compared with polycrystalline ice. A further fact is that the curves of $\tan \delta$ for single-crystal ice do not show a rapid increase as the temperature approaches the melting point, as they do in the case of polycrystalline ice, but on the contrary they fall steeply toward the melting point. Moreover there is probably no low-temperature peak of $\tan \delta$ as observed around -145°C in polycrystalline ice (or if a peak does exist, it is far smaller than in polycrystalline ice). We have only the $\tan \delta$ peak in the middle range, the peak that exhibits a frequency-dependent displacement toward the higher temperatures.

The rapid rise of $\tan \delta$ in polycrystalline ice as the melting point is approached, in contrast to the experimentally established decrease toward the melting point in single-crystal ice, may no doubt be ascribed to internal friction arising at the grain boundaries. To support this there is another experimental fact; it appears from curve (4) of Figure 5. This curve represents measurements made on a specimen comprising two single crystals separated by one grain boundary, as shown in the polarized-light photograph C of Figure 2. Branch a of curve (4), after passing through a maximum of height 0.01 (not shown in the Figure), joins the other branch a'. In this curve, then, as the Figure shows, there is a rise of $\tan \delta$ when the temperature exceeds -20°C . In other words, the presence of even a single crystal boundary in the specimen causes the temperature characteristics of $\tan \delta$ to resemble those of polycrystalline ice.

In Figure 6 we show other examples of measurements of $\tan \delta$ on single-crystal ice. Curves (3) and (4) of Figure 6 exhibit the temperature characteristics of $\tan \delta$ for a single crystal which, like the previous specimens, has the C-axis more or less coinciding with the lengthwise axis of the bar. The vibration frequencies are 715 and 1950 cycles respectively. In both cases the peak is small, about of the same size as in Figure 5, and the temperatures at which the peak appears are -40°C and -22°C . Curves (1) and (2) are an example of a single-crystal ice having a $\tan \delta$ maximum of the same height as that of polycrystalline ice. In this single crystal the C-axis is orientated in the direction of the thickness of the test-bar. Curve (1) is at 510 cycles, curve (2) at 1390 cycles. These two curves lack the rapidly rising part of $\tan \delta$ in the vicinity of the melting point; the peak in the vicinity of -145°C is also missing. The middle-range peak, the peak which with increasing frequency shifts toward higher temperatures, is markedly higher as compared with the single crystal of curves (3) and (4). This specimen, examined between crossed polarizers, shows up as entirely a single crystal, but there is a visible pattern of internal distortion (Figure 7). Such distortion is quite absent from the single crystal of curves (3) and (4), or from the single crystal of Figure 2. One may perhaps imagine the distortion pattern as an array of very slightly inclined faces of microscopic crystals, that is, of microscopic sub-grain boundaries. This is no more than simple speculation, though it is credible that the markedly greater size of the peak in curves (1) and (2), as compared with that in curves (3) and (4), should be due to internal distortion of the crystal. A final decision in this matter must wait upon future research.

Internal friction in single-crystal ice may be summarily described as follows. The $\tan \delta$ curve of single-crystal ice does not show the rise in the high-temperature range, the rise that is caused by crystal boundaries. The peak in the vicinity of -145°C is practically absent (or if present, is very small). The $\tan \delta$ peak that appears in the middle range of temperatures may be small, a few parts or a tenth of that of polycrystalline ice, or it may be of about the same height as in polycrystalline ice.

iii) Change in $\tan \delta$ due to Tyndall figures or internal strains produced in the ice by thermal irradiation. It is well known that internal friction in metals alters with working --- that is, it is modified by compressions and extensions. In the case of ice also it may be very informative to investigate how the internal friction, as discussed above, will alter with working, if the properties of ice are considered in analogy with metals. But since ice is characteristically frangible, it would be difficult to work it freely in the same way as a metal. Therefore we tried thermal irradiation of the ice, producing Tyndall figures by internal melting; then, after re-freezing, we made measurements of $\tan \delta$ and compared them with the prior values.

When ice is subjected to thermal irradiation, melting begins at the crystal boundaries, while at the same time there occurs, in the interior of the crystal grains, an internal melting in the form known as Tyndall figures or Tyndall's flowers [7]. Upon cessation of the irradiation, these melted regions re-congeal into ice, and when this happens the internal melt-water does not freeze in the same way as before: there remain vacuous bubbles, due to difference in the specific volumes of ice and water. Thus fissures are opened along the basal planes and distortion is produced. When examined in a dark room under oblique illumination, the Tyndall figures or the fine cracks in the basal planes shine strongly by reflected light. The Tyndall figures or fine cracks in the single-crystal ice of Figure 8, which has the C-axis in the lengthwise direction of the rod, are visible as a multitude of parallel lines. In this way, then, we can produce an internal distortion in ice.

Figure 9 shows the temperature-behavior of $\tan \delta$ as measured in polycrystalline and in single-crystal ice before and after exposure to thermal radiation. Curve 1 is for polycrystalline ice before irradiation and is measured at the fundamental vibration frequency of 460 cycles; curve 2 is for the same specimen after irradiation and development of the Tyndall figures. Let us first look at the $\tan \delta$ peak in the middle range of temperatures. The graph shows that this peak is quite unaffected by the irradiation. The peak in the vicinity of -140°C , however, has become smaller in comparison to its height before irradiation. And the grain-boundary internal friction that develops in the high-temperature range has, after irradiation, become markedly greater than before irradiation.

Curves (3) and (4) represent the result of similar experiments on single-crystal ice. Curve (3) is the variation of $\tan \delta$ before irradiation; curve (4) after irradiation. The two coincide almost perfectly; the internal friction of single-crystal ice is quite unaffected by distortions or Tyndall figures artificially produced within it.

From these two experiments, we may say as follows. The internal friction arising at crystal grain boundaries is markedly increased by thermal irradiation; the crystal grain boundaries are strongly modified by melting due to the

irradiation. But the frequency-dependent peak of $\tan \delta$ in the intermediate temperature range is unchanged, both in polycrystalline and in single-crystal ice. Consequently the mechanism here causing the internal friction is unrelated to macroscopic structures such as Tyndall figures or internal cracks; we may take it that the cause lies in a microscopic structure in the ice crystal. In polycrystalline ice the $\tan \delta$ peak at the low-temperature end is reduced to about half-size by the thermal irradiation. The reason for this is not clear, but it is difficult to see in it a mechanism of reduction of internal friction by Tyndall figures or cracks. Rather we may take it as more likely an annealing effect; the specimen is heated to 0°C by the irradiation. But this conclusion must wait upon future research.

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IV. Activation Energy

We have seen that in the interval from 0° to -180°C the internal friction of ice exhibits three causally different characteristic variations. In polycrystalline ice there is a friction arising at the crystal grain boundaries; there is a friction exhibiting the characteristic that its peak is displaced with increasing frequency toward the higher-temperature side; there is the low-temperature friction in the vicinity of -140° to -150°C which exhibits no frequency-dependent displacement of its peak. The internal friction of single-crystal ice is of the frequency-dependent type alone; neither the grain-boundary friction nor the low-temperature peak appears. In this section of our paper we shall discuss the activation energies derivable from the temperature characteristics of these frictions.

In Figure 10 we have the values of $\tan \delta$ for the polycrystalline ice of Figure 4 in the temperature range from 0° to -35°C , plotted as ordinates on a logarithmic scale against the reciprocals of the absolute temperatures as abscissae. The numbers of the curves correspond to those of Figure 4. If we look at the low-frequency curve (1), we see that between 0° and -25°C the plotted points lie on a straight line, satisfying the relationship

$$\tan \delta = \tan \delta_0 \exp \frac{-E_1}{RT} \quad (3)$$

Here E_1 is activation energy, R is the gas constant, T is absolute temperature, and $\tan \delta_0$ is a constant. At temperatures below -25°C , however, the measurements deviate from the straight line onto a curve. This is because another relaxation mechanism which appears in the middle-temperature range begins to be superimposed. Curves (2) to (4) reveal that this deviation from linearity due to the superimposition effect appears at progressively higher temperatures as the vibratory frequency increases. Thus when we are considering only the internal friction arising at the crystal grain boundaries, the plotted points should not be extended too far toward the lower temperatures. From the slope of the straight-line parts of the family of curves in Figure 10 we find the activation energy E_1 for the grain-boundary internal friction to be about 17-20 Kcal/mol.

Next let us consider the internal friction developed in the middle temperature range. In Figure 4 we have shown the temperature behavior of $\tan \delta$ with the vibratory frequency as parameter. The internal friction

exhibits a sharp central peak, from which it diminishes steeply on both the high-temperature and the low-temperature sides. It is not clear what the mechanism is, but it may be that on the high-temperature side the vibratory strain closely follows the variations of the external driving forces, without any time-lag, while on the low-temperature side, on the contrary, the strain is not able to follow the stress variations; the phase-difference between the stress and strain vectors may be maximum at just the temperature where the maximum of $\tan \delta$ appears. The phenomenon is formally similar to the case of an alternating electric field applied to the ice; the dipoles in the ice, turning to follow the direction of the electric field, do so with a lag and with resulting dielectric losses.

Figure 11 is a replot of Figure 4 to show the relationship of $\tan \delta$ to the vibratory frequency, with the temperature as the [fixed] parameter; the abscissa is the angular frequency $2\pi f$ in a logarithmic scale. $\tan \delta$ versus $\log \omega$ gives us a family of curves with almost symmetrical peaks. If we put ω_{\max} for the angular frequency at which this $\tan \delta$ peak occurs, the relaxation time is

$$\tau = \frac{1}{\omega_{\max}} \quad (4)$$

In Figure 12, which shows $\tan \delta$ against a logarithmic scale of $\omega\tau$, the plotted points are nicely distributed on either side of the well-known relaxation curve:

$$\tan \delta = \Delta_m \frac{\omega\tau}{1 + \omega^2\tau^2},$$

$$\Delta_m = 0.009.$$

In Figure 13 the relaxation times τ , calculated from equation (4), are plotted as ordinates, and the reciprocal absolute temperatures at which the peaks appear are taken as abscissae. The straight line (a) is for glacier ice; (b) is for commercial polycrystalline ice; (c) and (d) are for single-crystal ice. In each case the relation between τ and T^{-1} is linear, satisfying the relationship

$$\tau = \tau_0 \exp \frac{E_2}{RT}$$

Here E_2 is the activation energy of the relaxation mechanism producing the internal friction peak; τ_0 is a constant. E_2 is calculated from the slopes of these straight lines, and the lines all being parallel to each other, we find that E_2 is about 6 Kcal/mol.

If we now compare these values with those of other research-workers, the situation is as follows. (e) in Figure 13 shows the relationship of relaxation time to temperature as obtained by Kneser et al. [8] for round rods of single-crystal ice in torsional vibration. In this case the activation energy is 8.45 Kcal/mol. The temperature range for the measurements, however, was $0^\circ - 25^\circ\text{C}$. On (f) are plotted, against T^{-1} , the values found by Humbel et al. [9] and by Auty and Cole [10] for the relaxation time as determined from the dielectric loss peak in ice. The activation energy for the dielectric relaxation, as calculated from the slope of this line, is 13.25 Kcal/mol, about twice the activation energy obtained by us for the

mechanical relaxation. The dielectric relaxation phenomenon is ascribed to rotation of the ice-molecule dipoles. Regarding the mechanism responsible for the mechanical relaxation phenomenon as observed by us in the range -30 to 90°C , nothing definite can be said from comparison of activation energies alone, but it is a point worth noting that 6 Kcal/mol is about half the activation energy of evaporation, or equal to the activation energy required to break one molecular bond in ice.

Now we must mention the activation energy of the internal friction that develops in the vicinity of -140° to -150°C . This peak diminishes with increase of the vibrational frequency, and within the range of experimental error there is no variation of the temperature at which the peak occurs. Formally speaking, this means that the activation energy is infinitely great. In single crystals prepared in the laboratory, the peak in question either does not appear or is small. It is not observed at all in ice which, like glacier ice, has been produced by sintering under great pressures acting over a long space of time.

V. Conclusions

In measurements of the internal friction of polycrystalline and single-crystal ice in the temperature range 0° to -180°C , it was found that, in the case of polycrystalline ice, the $\tan \delta$ [component] ascribable to the crystal boundaries at first exhibited an abrupt decline in the range from 0°C to -30°C . This [component] is completely extinguished at temperatures below -30°C , and in the range from -30°C to -90°C a frequency-dependent internal friction develops. With further decrease of temperature this friction dies out, and another peak then develops in the vicinity of -140°C to -145°C . The temperature at which the last peak appears is independent of frequency. In single crystals and in glacier ice this peak is not observed.

After melting the ice specimens on which we made our internal frequency determinations, the electric resistance of the water was measured at room temperature. The specific resistance of the melt-water from both the polycrystalline ice and the single-crystal ice was the same, namely $8 \sim 10$ times that of repeatedly distilled water, if the specific resistance of the latter is taken as $1.3 \times 10^8 \Omega \cdot \text{cm}$. In other words, the content of impurities in either the single-crystal ice or the polycrystalline ice is about $8 \sim 10$ times the content in repeatedly distilled water.

The temperature characteristics of $\tan \delta$ for glacier ice are quite different from those of the commercial polycrystalline ice. It is very interesting to compare the experimental results set forth above, and we shall likely have more to say about them in a future publication.

The authors are grateful to Professor Takeo HORI; also to Professor Ukichirō NAKAYA of Hokkaidō University. The ice crystals used in the experiments were furnished by Mr. Gorō WAKAHAMA of our Institute, whose contribution to the success of our work we should like to note. We also take this opportunity to express our gratitude for useful discussion of this research with members of the Snow Research Group, Institute of Low Temperature Science, and the Crystal Plasticity Research Group at Hokkaidō University.

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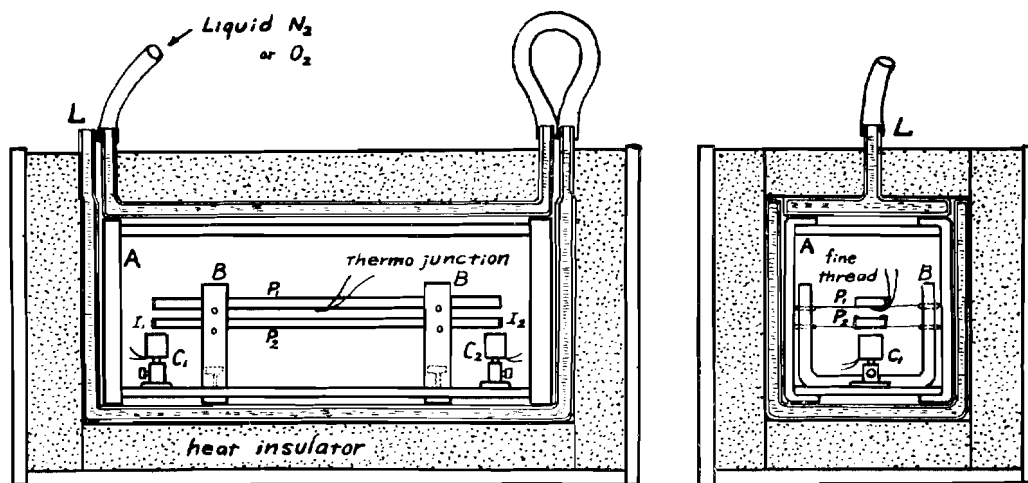


Fig. 1. Scheme of experimental apparatus.



Fig. 2. Patterns obtained with ice specimens put between crossed polaroids.

- A, B. Polycrystalline ice.
- C. 2-single crystal ice.
- D. Single-crystal ice.

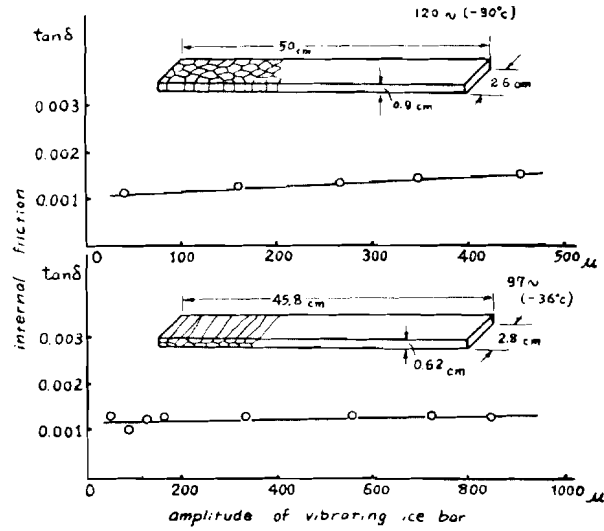


Fig. 3. Relation between $\tan \delta$ and amplitude of vibrating ice bar.

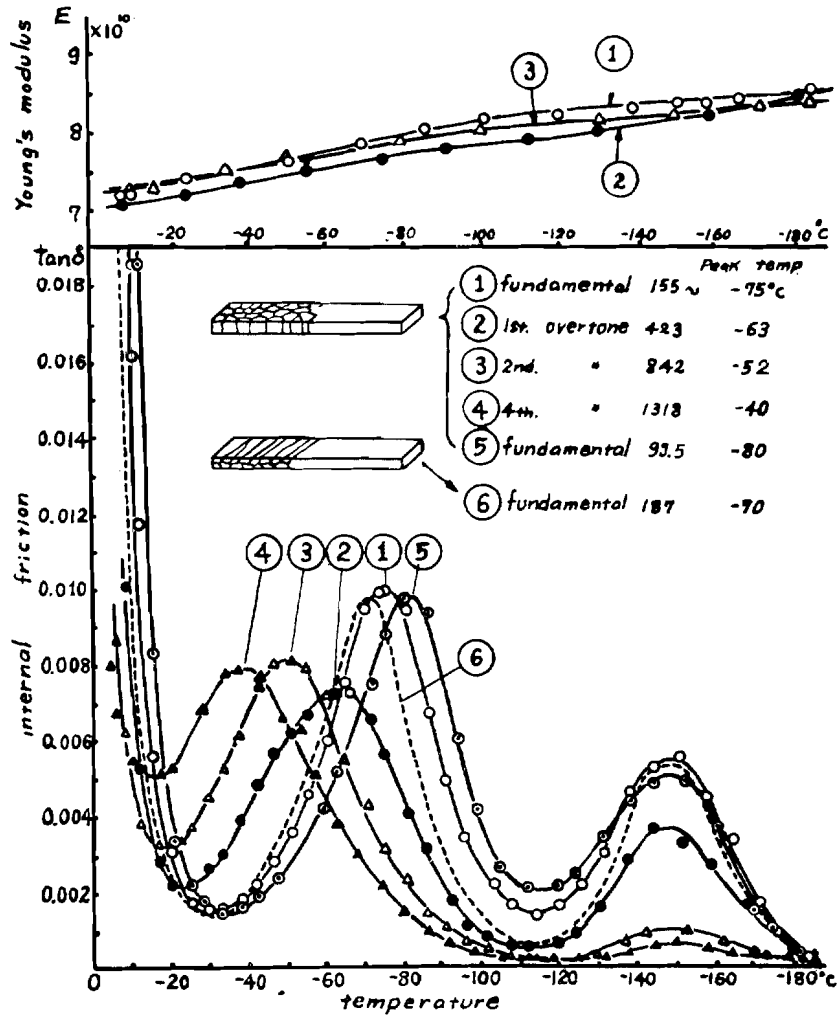


Fig. 4. Temperature dependencies of internal friction and Young's modulus of polycrystalline ice.

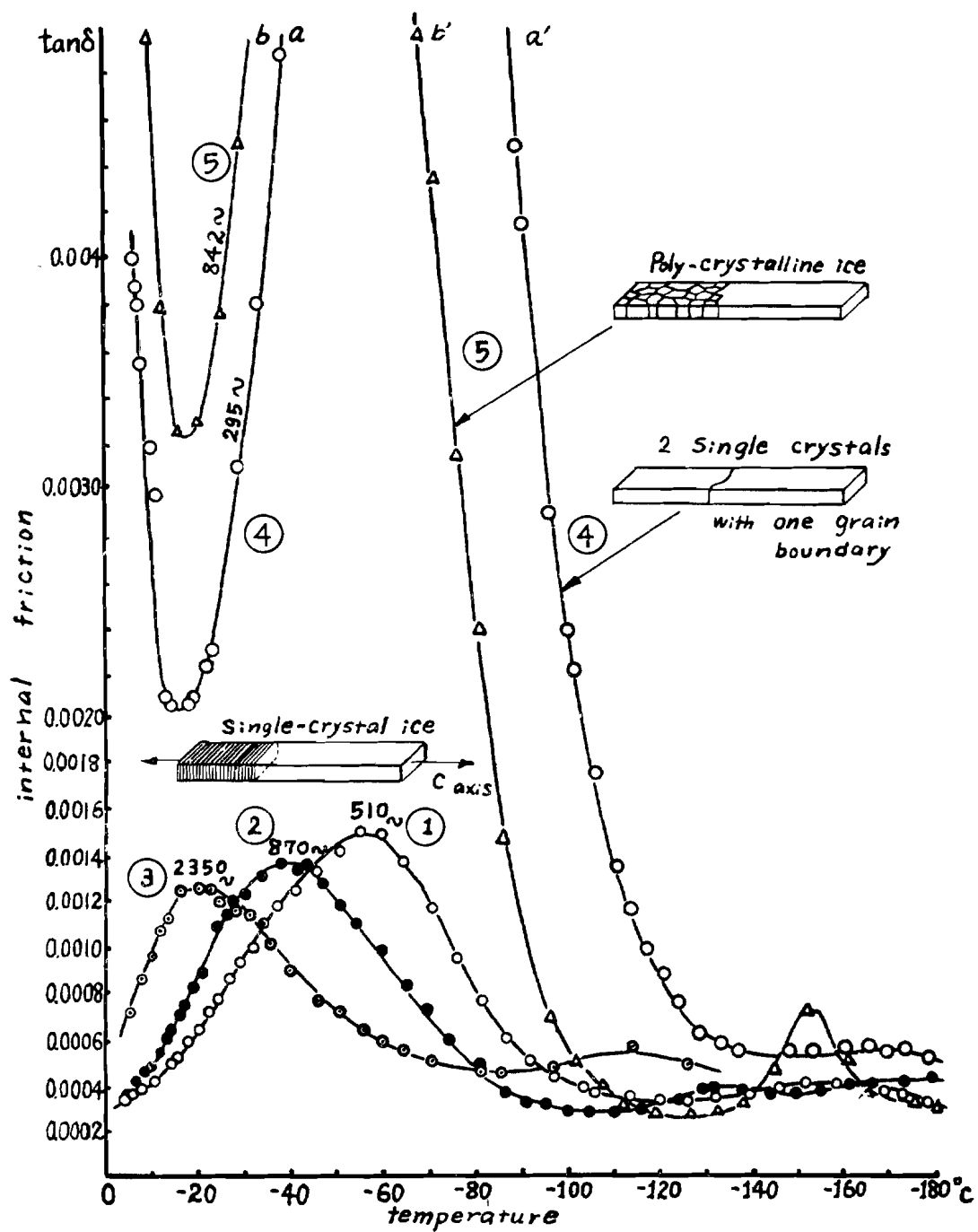


Fig. 5. Temperature dependencies of internal friction of single crystal ice.

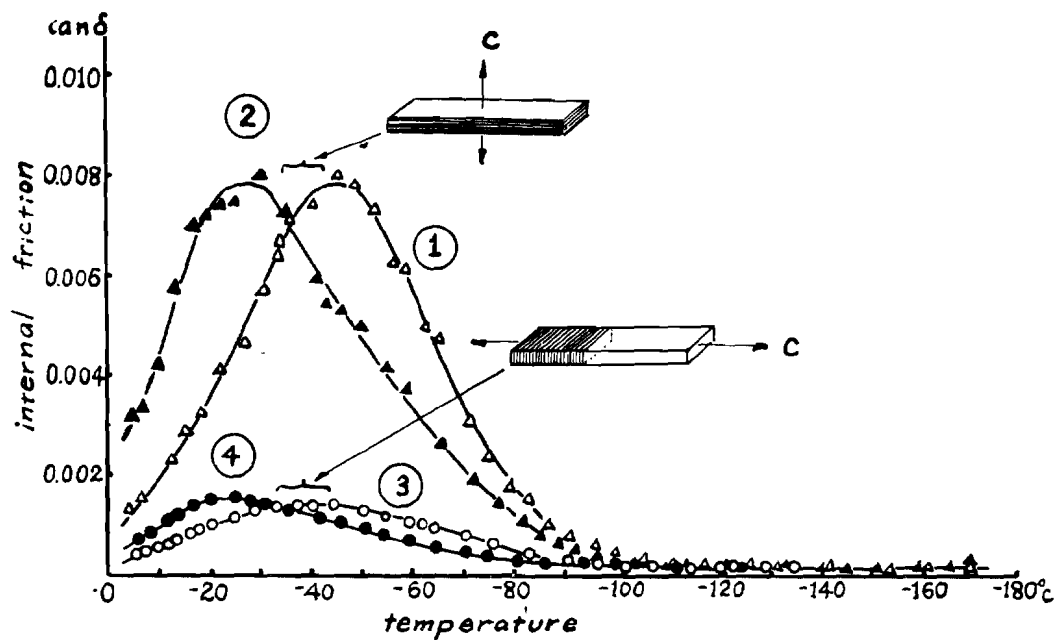


Fig. 6. Internal friction of two kinds of single crystal ice



Fig. 8. Tyndall's figure produced by heat radiation. (Single crystal ice)



Fig. 7. Single crystal ice having interior distortion. Photograph was taken under the crossed polaroids.

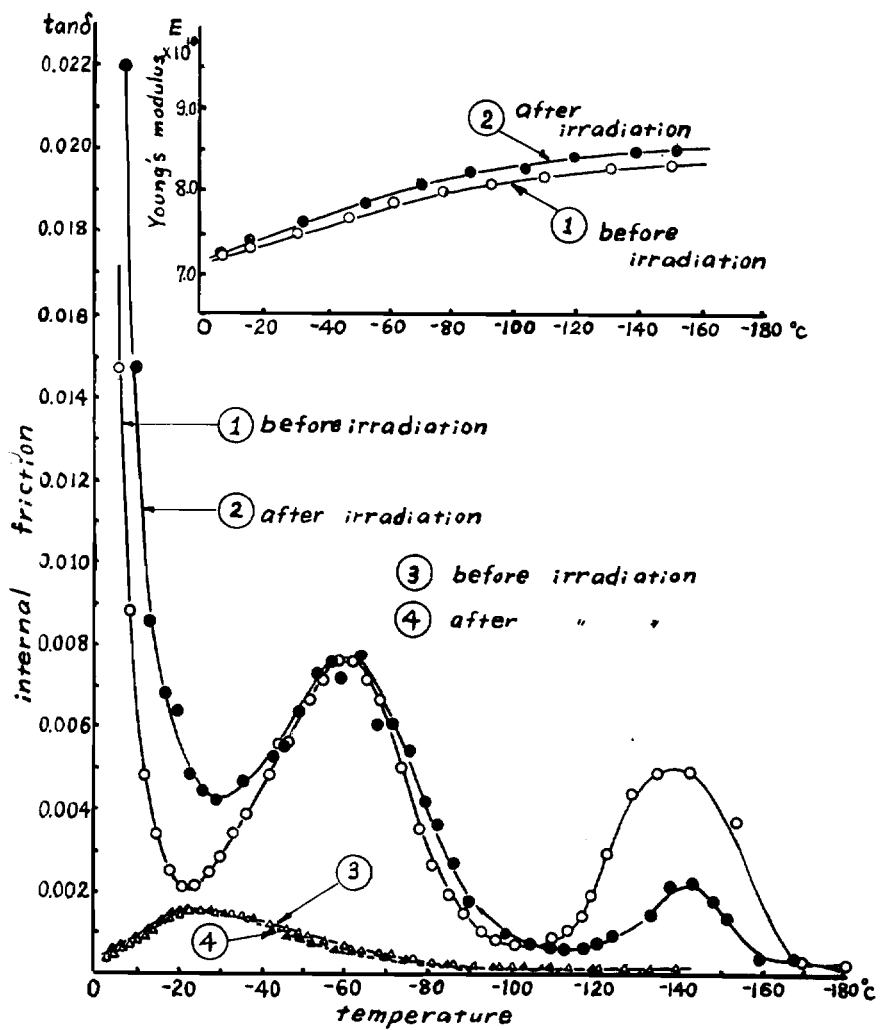


Fig. 9. Variation of internal friction due to irradiation with heat rays.

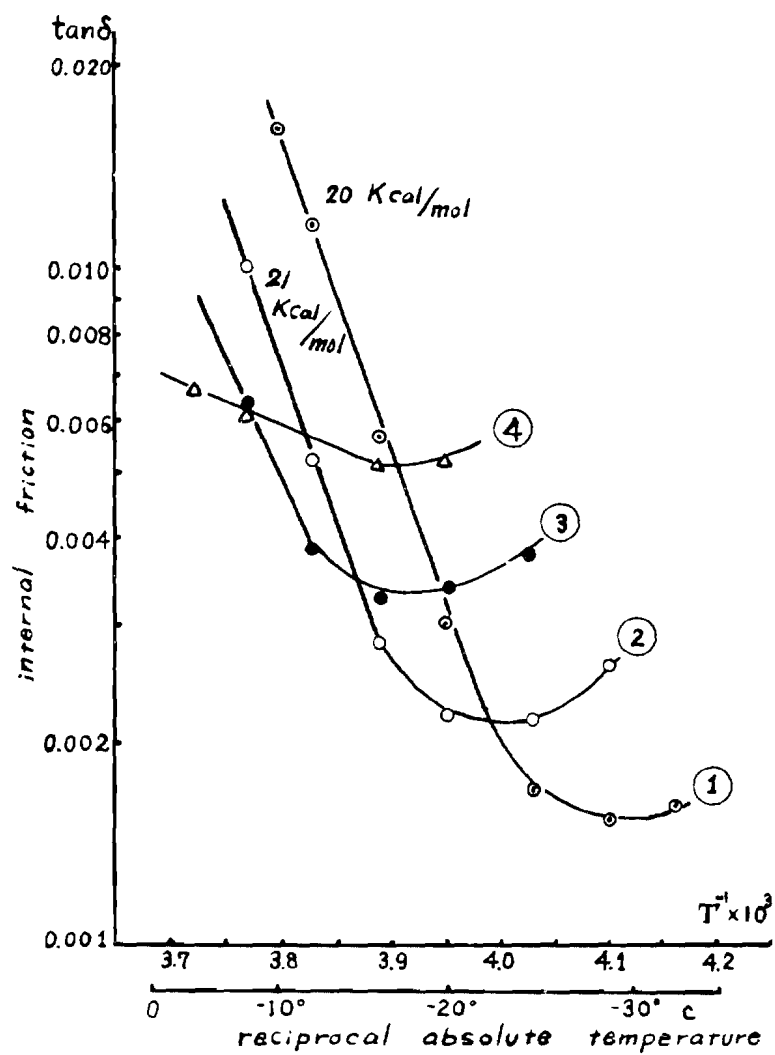


Fig. 10. Relation between $\log(\tan \delta)$ and reciprocal absolute temperature.

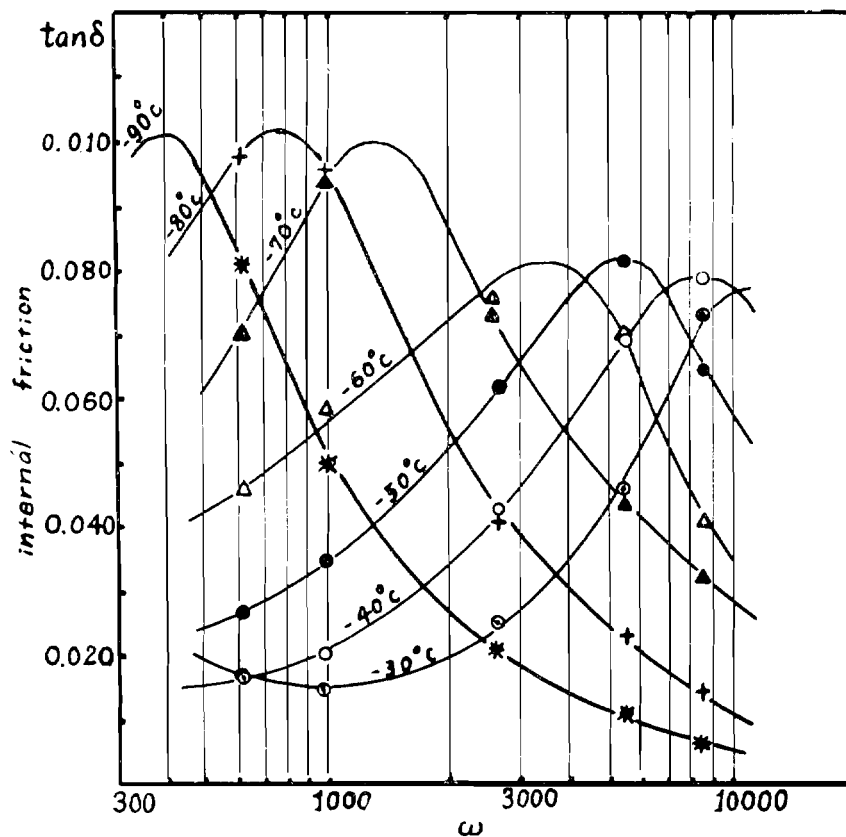


Fig. 11. Frequency dependence of internal friction of ice.
 ω in angular frequency.

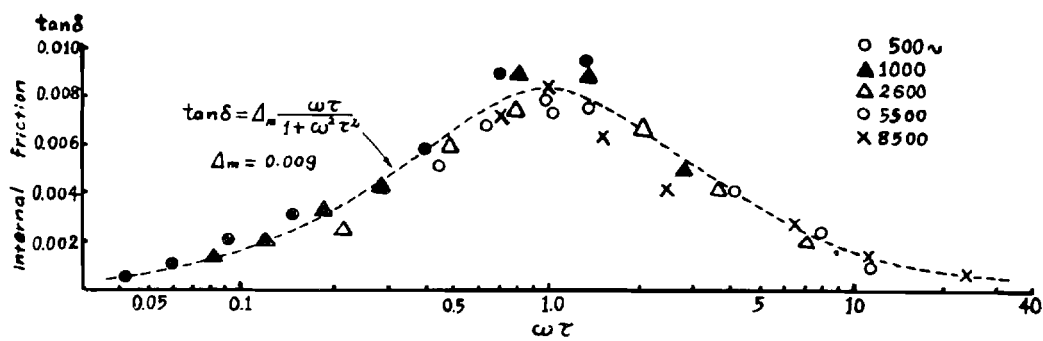


Fig. 12. Relation between $\tan \delta$ and $\omega \tau$.

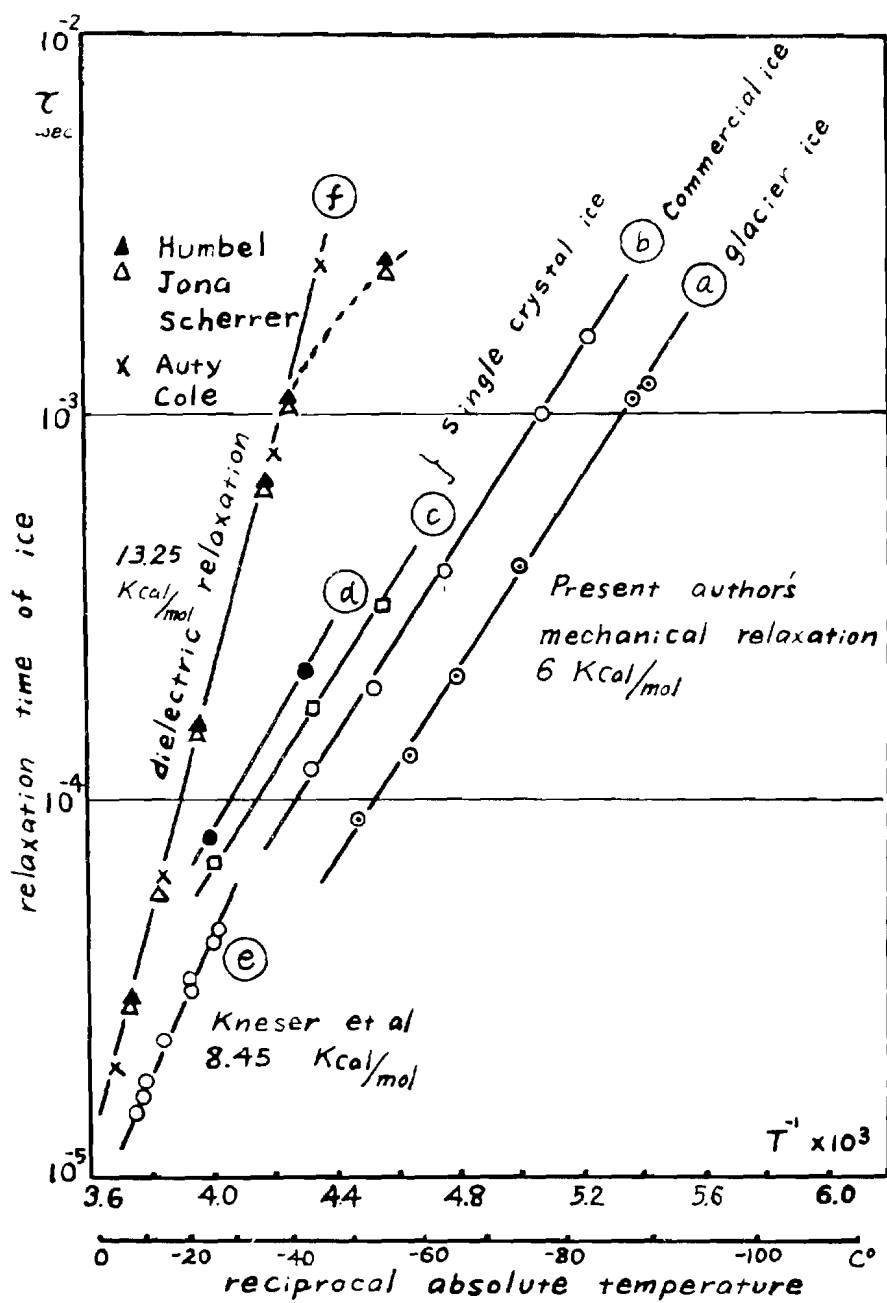


Fig. 13. Relation between relaxation time of ice and reciprocal absolute temperature.