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INELASTIC BEHAVIOUR OF ICE Ih SINGLE CRYSTALS IN THE LOW-FREQUENCY RANGE DUE TO DISLOCATIONS

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Abstract. The inelastic behaviour of ice Ih single crystals has been investigated by an inverted torsional pendulum in the low-frequency range. Three features are distinguished:

(i) a relaxation peak previously observed by several authors in the higher-frequency range,
(ii) an internal friction increasing with temperature in the high-temperature range (230–273 K),
(iii) within this high-temperature range, internal friction becomes amplitude dependent, and this dependence becomes greater the greater the temperature.

In this case, the internal friction has been interpreted in terms of movements of dislocations. Hence, the experimental results are interpreted with a model of internal friction based on an empirical relation for the velocity of dislocations. This model of internal friction is in fair agreement with experimental data. It is possible then to get an estimate of dislocation density. Hence it is shown that internal friction experiments can be useful in the study of the plastic behaviour of ice single crystals.

Résumé. *Rôle des dislocations dans le comportement inélastique basse fréquence de la glace Ih.* Le comportement inélastique de la glace Ih monocristalline a été étudié à l'aide d'un pendule de torsion inversé fonctionnant dans le domaine des basses fréquences. Il apparait trois caractéristiques:

(i) un pic de relaxation observé précédemment par divers auteurs dans le domaine des hautes fréquences,
(ii) un frottement intérieur croissant rapidement avec la température dans le domaine 230–273 K,
(iii) dans ce domaine de températures, le frottement intérieur dépend de l'amplitude de déformation et cette dépendance est d'autant plus forte que la température est plus élevée.

Nous nous sommes plus particulièrement intéressés dans ce travail au comportement de la glace monocristalline dans le domaine des hautes températures en mettant en évidence le rôle des dislocations. La comparaison de nos résultats avec ceux obtenus par topographie de rayons X nous permet d'interpréter l'ensemble des données apportées par le frottement intérieur. Il est alors possible d'obtenir une estimation de la densité de dislocation. Il apparaît ainsi que les mesures de frottement intérieur peuvent être utiles pour l'étude de la déformation plastique de la glace.

Zusammenfassung. *Anelastisches Verhalten von Eis-Ih-Einkristallen im Niederfrequenzbereich aufgrund von Versetzungen.* Das anelastische Verhalten von Eis-Ih-Einkristallen wurde mit einem umgekehrten Torsionspendel im Niederfrequenzbereich untersucht. Drei Merkmale werden herausgestellt:

(i) Ein Relaxationsdämpfungsmaximum, das bereits früher von verschiedenen Verfassern im höheren Frequenzbereich beobachtet wurde.
(ii) Ein Anstieg der inneren Reibung mit der Temperatur im Hochtemperaturbereich (230–273 K).
(iii) Innerhalb dieses Hochtemperaturbereiches wird die innere Reibung amplitudenabhängig, und diese Abhängigkeit wird grösser je höher die Temperatur.

Die innere Reibung wurde in diesem Fall mit Hilfe von Versetzungsbewegungen gedeutet. Die experimentellen Befunde werden daher mit einem Modell der inneren Reibung erklärt, das auf einer empirischen Beziehung für die Versetzungsgeschwindigkeit beruht. Dieses Modell der inneren Reibung stimmt mit den experimentellen Werten gut überein. Es ist damit möglich eine Abschätzung der Versetzungsdichte zu erhalten. Daraus lässt sich folgern, dass Experimente der inneren Reibung bei der Untersuchung des plastischen Verhaltens von Eis-Einkristallen nützlich sein können.

1. Introduction

The inelastic behaviour of ice single crystals has been studied with a torsional pendulum in the low-frequency range (1 Hz) (Vassoille and others, 1974), where, in the temperature range 100 to 273 K, three noteworthy features were observed (Figs 1 and 2):

(i) a relaxation peak previously observed by several authors in higher frequency ranges (Schiller, 1958; Kuroiwa, 1964).
(ii) an internal friction which increases with temperature in the high-temperature range (230–273 K).
(iii) in the high-temperature range, internal friction becomes amplitude dependent. The higher the temperature, the more pronounced this amplitude dependence.

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The relaxation peak is generally considered in terms of the reorientation of water molecules during the application of cyclic stress (Bass, 1958; Gosar, 1974). This peak is described by the well known Debye relation.

The present work will deal only with the high-temperature internal friction of ice single crystals in order to show the role of dislocations. In this temperature range the dislocation mobility increases rapidly with temperature. When a shear stress is applied, dislocations can move for a short distance inducing a deformation which lags in phase behind the stress

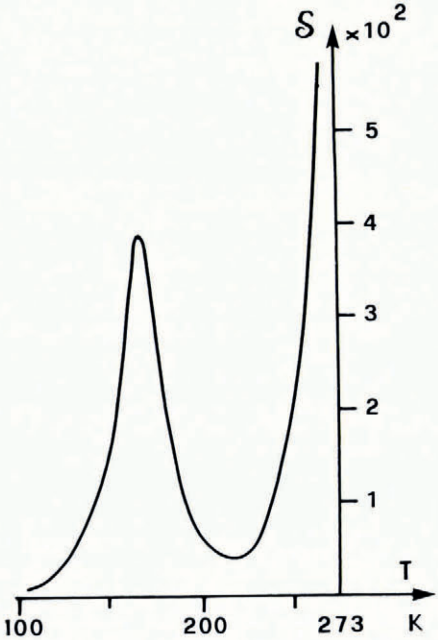

Fig. 1. Internal friction as a function of temperature.

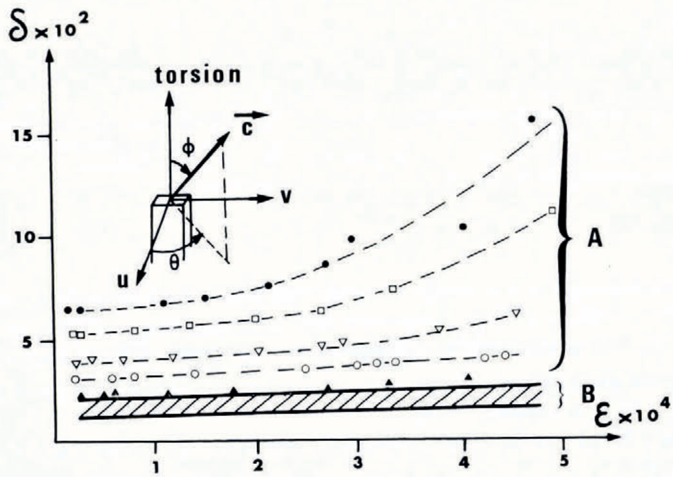

Fig. 2. Internal friction as a function of maximal strain amplitude at several temperatures. The shaded band contains all the results obtained between 260 and 272 K with a single crystal for which $\theta = 45°$, $\phi = 87°$. The other curves are obtained with a single crystal for which $\theta = 24°$, $\phi = 16°$: ● 272.5 K, □ 269.5 K, ▽ 267.5 K, ○ 264.5 K, ▲ 261 K.

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(damping), a phenomenon generally observed with other crystalline materials. The modifications of this high-temperature inelastic behaviour of ice single crystals produced by plastic deformation or doping with HF were examined. The interpretation of the experimental data has been sought in terms of an empirical relation for the velocity of dislocations.

2. Experimental procedure

Measurements were made with an inverted torsional pendulum in the low-frequency range. Variations in the logarithmic decay of oscillations versus temperature are automatically recorded (Etienne and others, 1975). The amplitude of oscillations is variable: thus, measurements of internal friction as a function of strain amplitude are possible. Specimens in the form of rectangular bars (8 mm × 2 mm × 76 mm) were mechanically cut from single-crystal blocks grown by the Bridgman method. Measurements were directly made with: freshly grown ice, plastically strained ice, or HF-doped ice. Plastic deformation is obtained by torsional creep at 265 K. The diffusion coefficient of hydrogen fluoride in ice being very high (Fletcher, 1970, p. 161), this property is used for doping the specimens by covering them with an HF solution. The HF concentration is estimated by electrical resistivity of the melted specimen. Moreover, the displacement of the relaxation peak (Vassoille and others, 1977) confirms the result. Crystallographic orientation of specimens and dislocation density were determined by X-ray techniques.

3. Experimental results

In addition to the previously observed relaxation peak, low-frequency experiments have shown another damping phenomenon above 230 K (Fig. 1): at these higher temperatures, as well as the normal increase of internal friction with temperature, δ becomes amplitude

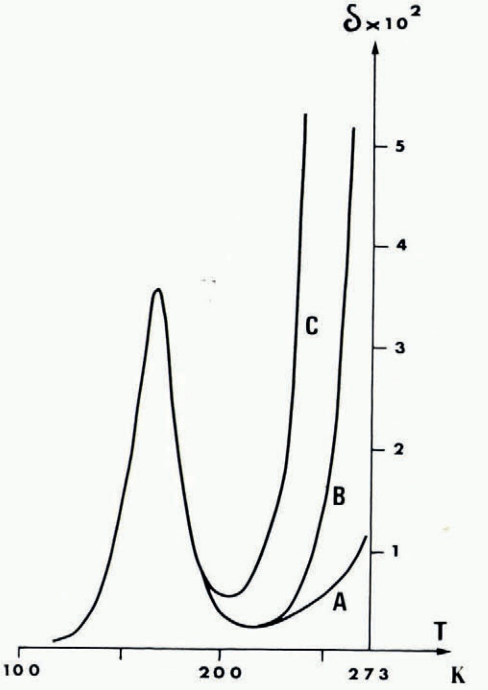

Fig. 3. Influence of plastic deformation: A. undeformed ice, B. after 0.5% straining, C. after 2.5% straining.

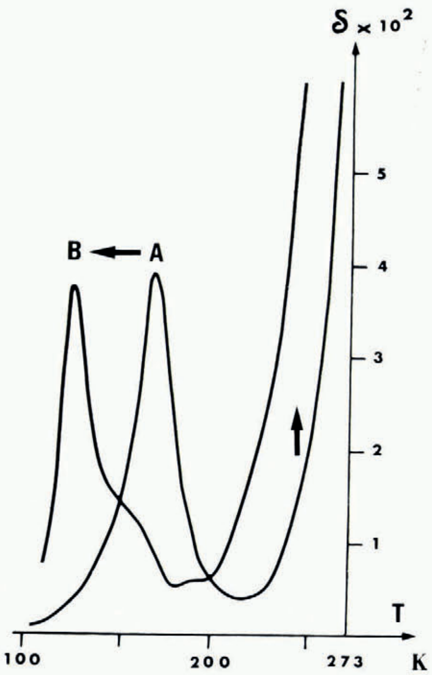

Fig. 4. Internal friction as a function of temperature for a single crystal of ice Ih: A. pure ice, B. HF-doped ice.

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dependent. As is shown in Figure 2, this amplitude dependence is maximum when the torsional axis is parallel to the *c*-axis.

It can be seen that this high-temperature internal friction increases as plastic strain is increased (Fig. 3), whereas the relaxation peak is not affected by plastic deformation as also observed by Kuroiwa (1964). This evidence supports the view that mechanical relaxation phenomena observed in ice are not due to the movements of dislocations (VanDevender and Itagaki, 1973).

When ice is doped with HF (Fig. 4), the relaxation peak is observed at lower temperatures than in the case of pure ice, and in addition the high-temperature internal friction is increased and becomes more amplitude dependent (Fig. 5). Furthermore, the amplitude dependence appears at lower temperatures than in the case of pure ice (the HF concentration obtained from the shift of the relaxation peak is: 20±5 p.p.m.).

4. Discussion

The inelastic behaviour of ice Ih in the high-temperature range is interpreted in terms of dislocation movements. Thus, it is necessary to describe models of dislocation glide in ice. Then the internal friction induced by the movement of these linear defects can be calculated and the result compared with experimental data.

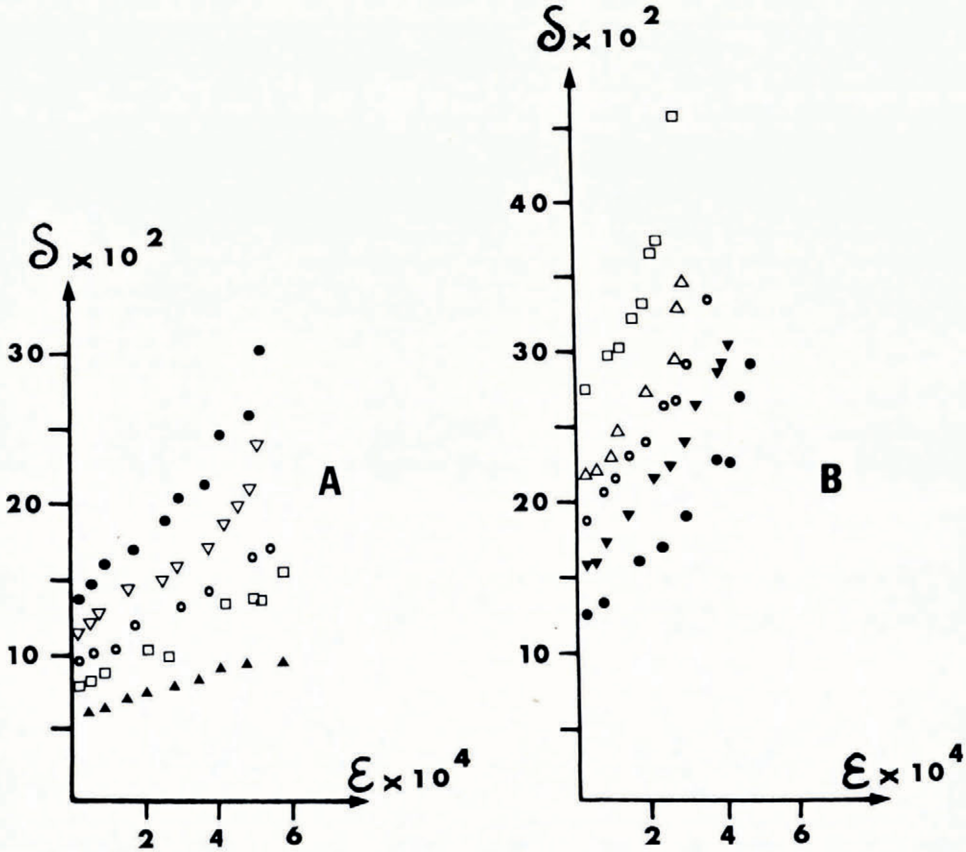

Fig. 5. Influence of HF doping on the amplitude-dependent internal friction. A. pure ice: ● *272.5 K,* ▽ *271 K,* ○ *269 K,* □ *267 K,* △ *264 K. B. HF-doped ice:* □ *272 K,* △ *269.5 K,* ○ *267 K,* ▽ *264 K,* ● *260 K.*

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4.1. *On the dynamic behaviour of dislocations in ice: a summary*

The experimental study of the plasticity of ice, and observations of etch pits or X-ray topography show that ice plasticity is connected with dislocation movement in the basal plane. These dislocations have Burgers vectors such as $b = \frac{1}{3}a\langle 11\bar{2}0\rangle$. The glide of these dislocations takes place by breaking bonds and forming other bonds. Glen (1968) suggested this formation of new bonds is only possible if H_2O molecules are correctly orientated. This idea has been quantitatively developed by several authors (Perez and others, 1975; Whitworth and others, 1976; Frost and others, 1976). The velocity of a dislocation v_d is generally given at low stresses by:

$$v_d = AN_k \frac{b^5}{kT} \frac{\tau}{\tau_r}, \tag{1}$$

where A is a numerical coefficient $(1 < A < 8)$, N_k the concentration of kinks along the dislocation, and τ_r the relaxation time associated with water-molecule rotation.

At higher stresses, thermal activation of double kinks must be taken into account and the following expression has been proposed

$$v_d \propto P(\tau), \tag{2}$$

the factor $P(\tau)$ shows a stress dependence which is nearly exponential. However this model is not satisfactory since the stress dependence at high stresses is not properly described, nor can the HF doping effect be satisfactorily explained by this model. Furthermore, X-ray topographic measurements show the dislocation velocity in ice to increase both with stress and temperature but as the temperature increases, the stress dependence becomes relatively higher. These results can be described by the empirical relation:

$$v_d = A \exp\left(-\frac{U_a}{kT}\right) \tau^{\frac{1}{2}} \sinh \alpha\tau^{\frac{1}{2}}. \tag{3}$$

This relation corresponds to a linear variation of v_d with τ only when τ or α (or, strictly, $\alpha\tau^{\frac{1}{2}}$) has a low value. U_a is an apparent activation energy to which it is difficult to give a physical meaning. The results of Maï (1976) lead to the values $A = 54.3\times 10^2$, $U_a = 0.55\pm 0.05$ eV, while α varies from 10^{-3} (at 251 K) to 3×10^{-3} (at 270 K).

4.2. *Calculation of the internal friction*

The logarithmic decrement is given by:

$$\delta = \frac{\Delta W}{2W},$$

with $\Delta W = \oint \tau \,\mathrm{d}\epsilon$, the energy dissipated during one cycle of sine stress, and $W = \tau_0^2/2G$, the maximum elastic energy during this stress cycle.

The strain-rate of a crystal having dislocation density ρ_d is given by:

$$\dot{\epsilon} = \rho_d v_d b.$$

If the sinusoidally varying stress is given by $\tau = \tau_0 \sin 2\pi\nu t$ we obtain:

$$\delta = \frac{G\rho_d b}{\tau_0} \oint \sin(2\pi\nu t)\, v_d \,\mathrm{d}t. \tag{4}$$

In an earlier paper, it was proposed (Perez and others, 1975) that

(i) kink diffusion induces amplitude-independent internal friction δ_1 (Equation (1) is used to calculate Equation (4));

(ii) thermal activation of double kinks induces temperature- and amplitude-dependent internal friction δ_2 (Equation (2) is used to calculate Equation (4)).

Actually, the result obtained for high-amplitude stresses or after HF doping have shown that this suggestion is not in good agreement with all the experimental data. Hence, Equation (4) has been calculated using the empirical relation in Equation (3). The result was simplified to:

$$\delta \simeq \delta(0, T)\,\frac{\sinh \alpha\tau_0^{\frac{1}{2}}}{\tau_0^{\frac{1}{2}}}, \tag{5}$$

where

$$\delta(0, T) = \frac{AG\rho_d b}{2\nu}\exp\left(-\frac{U_a}{kT}\right). \tag{6}$$

$\delta(0, T)$ is proportional to the dislocation density ρ_d. At low stresses, Equation (5) can be simplified and one has

$$\delta \approx \alpha\delta(0, T). \tag{7}$$

Thus, it can be concluded that there is only one type of internal friction which is both stress and temperature dependent and which is due to the movement of dislocations in ice; at low stresses, this internal friction depends only on temperature (Equation (7)) but as the temperature increases the stress dependence becomes relatively higher (Equation (5)).

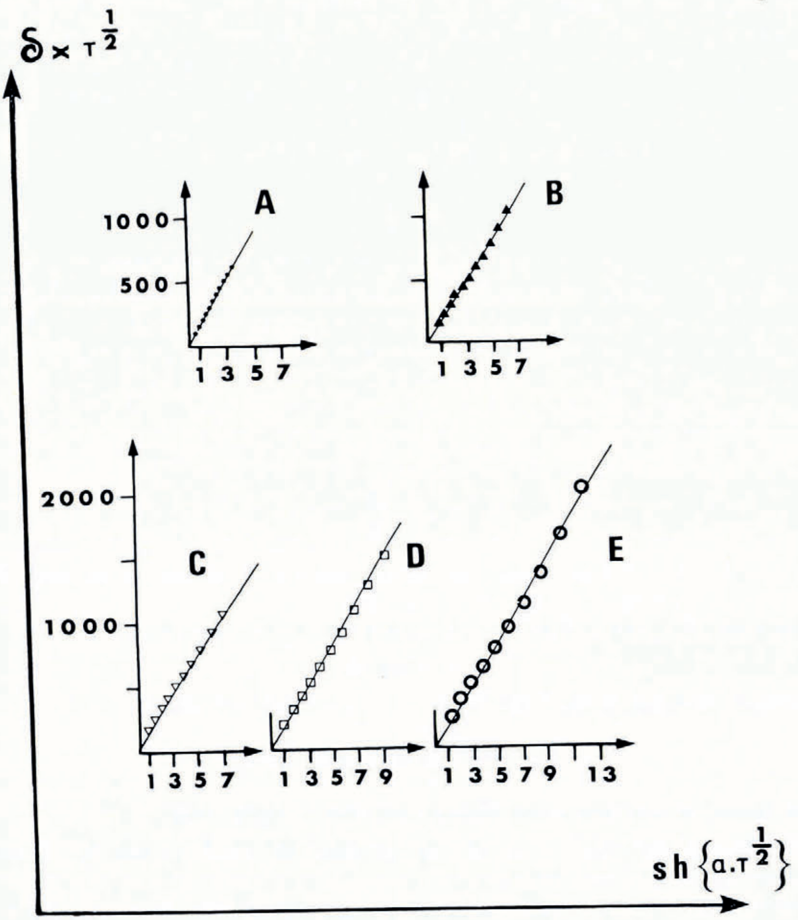

Fig. 6. Variations of $\delta\tau^{\frac{1}{2}}$ plotted against sinh $(\delta\tau^{\frac{1}{2}})$ for pure ice: A. 264 K, B. 267 K, C. 269 K, D. 271 K, E. 272.5 K.

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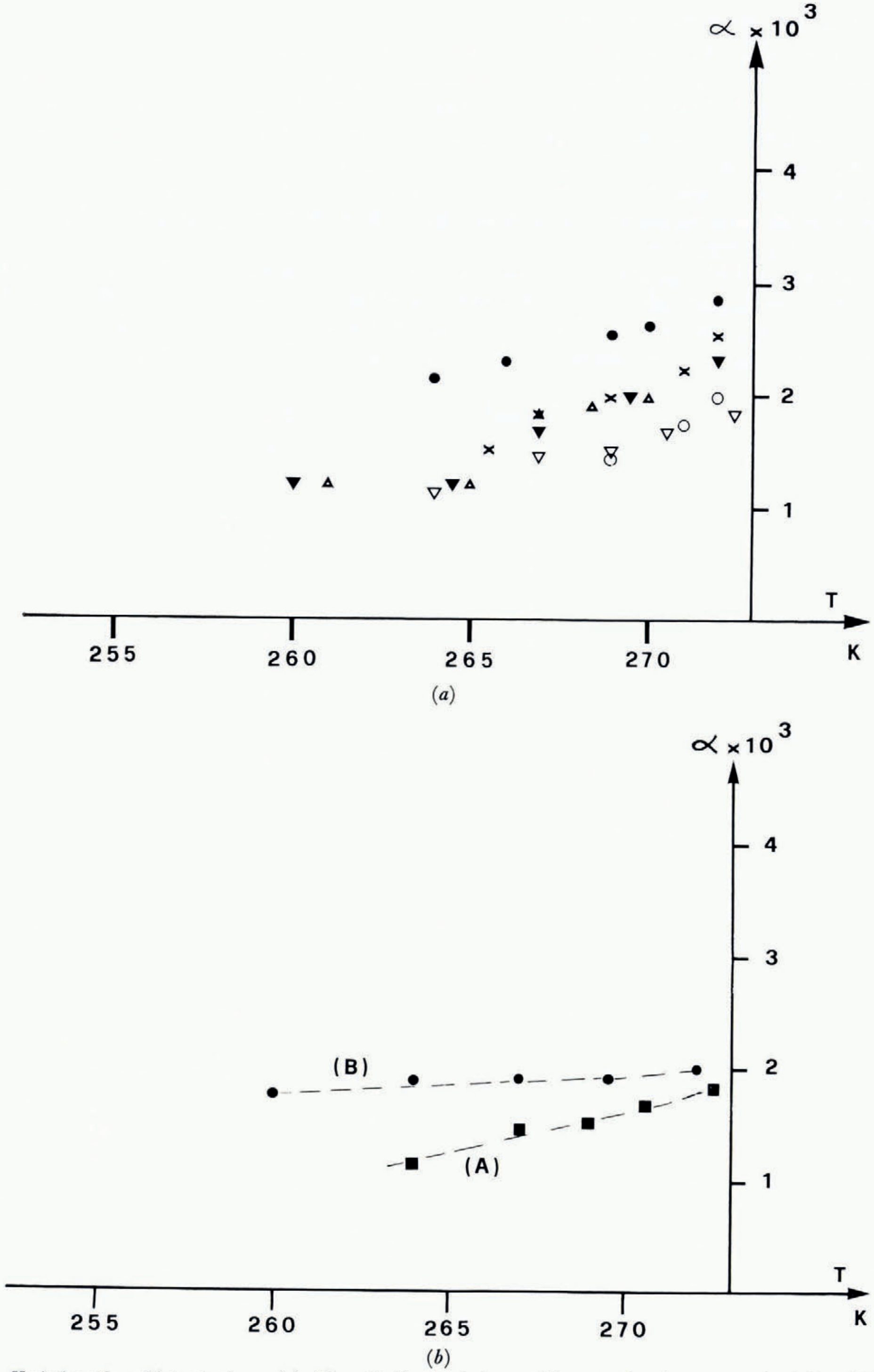

Fig. 7. Variation of α with temperature. (a) All results for six specimens, (b) comparison between pure ice (A) and HF-doped ice (B).

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4.3. *Comparison with experimental data*

After measuring the internal friction as a function of amplitude, local internal friction has been calculated from global results (e.g. Figs 2 and 5) which corresponds to a specimen with a stress gradient as indicated by Perez and others (1965). Then, after transformation of the curves in Figure 5, it has been asserted that it is possible to find such values of α that straight lines are obtained in a plot of $\delta\tau^{\frac{1}{2}}$ against sinh $\alpha\tau^{\frac{1}{2}}$ (Fig. 6). The variations of α with temperature is shown for six different specimens in Figure 7(a). In spite of the scatter, the values appear to be in good agreement with those obtained by X-ray topographical measurements and increase with temperature.

In the case of HF-doped ice, the same theoretical treatment applied to the experimental data leads to an higher value of α. Moreover, this value is less temperature dependent than in the case of non-doped ice (Fig. 7(b)). Such a result is again in accordance with those obtained by C. Maï and co-workers from X-ray topographic observations made with HF-doped

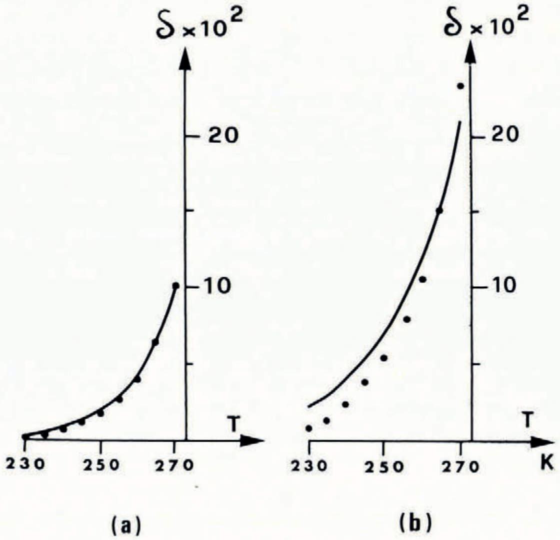

Fig. 8. High temperature internal friction; the full line is the experimental curve, the points plotted are theoretical values: A. pure ice, B. HF-doped ice.

TABLE I. DISLOCATION DENSITIES ρ_d IN cm/cm³

(a) *Internal friction measurements*

Specimen	*Initial density*	*Density after plastic deformation*	*Density when HF doped*
G_{21}	5.0×10^5	(4.8%) 1.5×10^7	—
G_{22}	3.5×10^5	(2.1%) 10^7	—
G_{31}	5.0×10^5	(0.8%) 4.5×10^6	—
G_{32}	4.0×10^5	(7.0%) 2.5×10^7	—
Grenoble, June 1976	4.0×10^6	—	7×10^6

(b) *Comparison between X-ray topographic and internal friction data*

Laboratory:	E.T.H., Zürich	Institut de Glaciologie, Grenoble	Department of Environment, Ottawa
Growing method:	modified Bridgman method	modified Bridgman method	melting-zone method
X-ray topography:	$10^{4\pm1}$	$10^{5\pm1}$	$10^{3\pm1}$
Internal friction:	10^6	3×10^5 to 4×10^5 (5 samples of part (a) above)	6×10^5

ice. Equation (7) has been used to describe the low-stress temperature-dependent internal friction (Fig. 1). A value of $U_a \approx 0.41$ eV was obtained, but this value may vary from one specimen to another, and the results obtained with 70 samples corresponding to different ice single crystals are in the range:

$$0.33 \text{ eV} \leqslant U_a \leqslant 0.53 \text{ eV},$$

depending on the history of the ice single crystal and the specimens. These values decrease after HF doping, for instance, in the case of the specimen corresponding to the curves shown in Figure 4, $U_a = 0.30$ eV after HF doping. This value has to be compared to the one obtained before HF doping, i.e. 0.41 eV.

From Equation (6), values of ρ_d can be calculated for different specimens with the corresponding values of U_a and A. These values are shown in Table I from which several conclusions can be drawn:

(i) the calculated value of ρ_d is sensibly higher than that directly measured by X-ray topography. As the mounting of the specimens in the pendulum needs mechanical machining, dislocation density might have been increased, especially on the surface; on the other hand, it was possible to use chemical cutting for specimens used for X-ray topography and so the accidental multiplication of dislocations is less probable.

(ii) the dislocation density is increased by plastic deformation; this increase depends on strain ratio.

(iii) HF doping also leads to an increase of the dislocation density; this result is in agreement with X-ray topographic observations (Jones and Gilra, 1973). So it appears that HF doping leads to an increase of both velocity and density of dislocations.

5. Conclusion

The present investigation has clearly shown the influence of dislocations in the inelastic behaviour of ice single crystals in the high-temperature range. Indeed, this inelastic behaviour is very similar to the behaviour of dislocations in the same range of temperature and stress observed by X-ray topography. Thus it is possible to use internal friction measurements to obtain results on linear defects which are useful for the analysis of the physical or mechanical behaviour of ice. Nevertheless, a description of the process of dislocation glide in ice is needed to improve the analysis of our internal friction data.

Acknowledgements

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DISCUSSION

C. R. Bentley: At what frequency were the torsional experiments carried out?

R. Vassoille: The experiments were done with a torsional pendulum and the frequency was about one Hertz.

J. W. Glen: Following Dr Jones' comment on the previous paper, it would seem desirable to do measurements of anelastic behaviour on crystals doped with dopants that do not increase the creep rate—they should presumably dissolve in the core and increase its size and might have been expected to increase velocity of individual dislocations. Your technique would seem to be capable of sorting this out.

Vassoille: We agree about the interest in such experiments and we hope to have the possibility of doing them in the near future. Nevertheless, the dissolution in the core of dopants, whatever they are, is not evident; furthermore as dopants can precipitate, it may be that they form obstacles to dislocation glide. In such a case, the suggested experiments would give results depending on both the increase of the size of cores and the effect of obstacles.

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