

DYNAMIC BEHAVIOUR OF DISLOCATIONS IN HF-DOPED ICE Ih

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ABSTRACT. A model of dislocation glide in ice Ih was recently proposed. This model was developed on certain assumptions, namely that transitions occur through cooperative movements of H₂O molecules in the non-crystalline core of dislocations. A relation between the velocity v_d of linear defects and shear stress τ or temperature T is obtained. This relation shows that v_d varies linearly with τ at low values of τ and (or) T but varies more rapidly at higher stresses; this non-linearity is more pronounced the higher the temperature. Such an analysis is extended in order to take into account doping effects. The case of HF-doped ice is considered: it is shown that there is a strong accumulation effect of HF molecules in the dislocation cores, which induces an increase of the rate of transitions. The results are in agreement with experimental data concerning both the velocity of dislocations and high-temperature internal friction in HF-doped ice.

RÉSUMÉ. *Comportement dynamique des dislocations dans la glace dopée à HF.* Un modèle de glissement des dislocations dans la glace Ih a été proposé récemment à partir des deux hypothèses suivantes: Les dislocations présentent un coeur étendu de matière non cristalline. Des transitions entre différentes configurations se produisent grâce à des mouvements coopératifs de molécules d'eau. Une relation entre la vitesse v_d des dislocations, la contrainte τ et la température T , a été obtenue; celle-ci montre que v_d varie linéairement avec τ aux faibles valeurs de τ et (ou) de T . Cette variation est plus rapide aux fortes contraintes et la non linéarité est d'autant plus importante que la température est élevée. Cette description a été développée de façon à rendre compte des effets dus au dopage. Le cas de la glace dopée à HF est étudié: un effet de ségrégation des molécules HF dans le coeur des dislocations pourrait provoquer un accroissement de la vitesse de transition. Une telle analyse est en accord avec les données expérimentales concernant tout aussi bien la vitesse des dislocations que le frottement intérieur haute température mesurés dans le cas de glace dopée à l'acide fluorhydrique.

ZUSAMMENFASSUNG. *Dynamisches Verhalten von Versetzungen in mit HF verunreinigtem Ih-Eis.* Für das Gleiten längs Versetzungen in Ih-Eis wurde jüngst ein Modell entwickelt. Dieses Modell beruhte auf gewissen Annahmen, nämlich dass Übergänge durch kooperative Bewegungen von H₂O-Molekülen im Kern der Versetzungen auftreten. Zwischen der Geschwindigkeit v_d linearer Defekte und der Scherspannung τ oder Temperatur T besteht eine Beziehung. Diese Beziehung zeigt, dass v_d bei kleinen Werten von τ und (oder) T sich mit τ linear verändert, jedoch schneller bei höheren Spannungen; diese Nichtlinearität ist umso ausgesprochener, je höher die Temperatur ist. Eine derartige Analyse wird auf den Fall von Verunreinigungseffekten erweitert, hier auf die Verunreinigung mit HF (Fluorwasserstoff). Es zeigt sich, dass sich eine starke Akkumulation von HF-Molekülen in den Versetzungskernen einstellt, die ein Anwachsen der Übergangsrates bewirkt. Die Ergebnisse passen gut zu experimentellen Daten, sowohl hinsichtlich der Versetzungsgeschwindigkeit wie der inneren Reibung bei hoher Temperatur in HF-verunreinigtem Eis.

1. INTRODUCTION

In a previous paper (Perez and others, 1978) a new model describing the dynamic behaviour of dislocations in ice was proposed. This model was developed making certain assumptions:

- (i) Dislocations have a non-crystalline extended core: the free energy of an ice crystal containing a dislocation of unit length is lowered by a value of ΔG when a non-crystalline arrangement of H₂O molecules can exist around the dislocation line, resulting in core energy and elastic energy being suppressed; the dimensions r^* of this non-crystalline molecular arrangement is limited by the increase of entropy of configuration and by the energy of the interface between crystalline and non-crystalline domains. This description is very similar to the concept of "heterophase dislocations" developed by Glicksman and Vold (1972).

- (ii) Rearrangements of H_2O molecules in the core of dislocations occur through configurational modes of excitation. The mean time τ_1 for a molecule to rearrange is dependent on fluctuations in the concentration of broken bonds C and can be taken equal to (Angel, 1971)

$$\tau_1 \approx \tau_0 \exp(1/C). \quad (1)$$

Assuming a linear distribution of the number of bonds in terms of their energy, it was found that

$$C = \gamma(kT/E)^2,$$

where E is the difference between the most probable potential energy of bonds in the non-crystalline core and that corresponding to the broken bonds, γ is a numerical factor equal to $\pi^2/6$ when $E > kT$ and about $\frac{3}{2}$ when E is between 0.10 and 0.15 eV.

- (iii) H_2O molecules may be constantly exchanging between the crystalline and non-crystalline regions; when no stress is applied the mean position of dislocations does not vary, but when a stress τ is applied, there is a transformation into non-crystalline ahead of the dislocation and "recrystallization" behind it through thermal fluctuations. Then the dislocations can glide after active configurations corresponding to a saddle-point are obtained through the correlated movement of n H_2O molecules. Since the loose structure of ice implies a small value of the correlation length, the frequency of formation of such activated configuration can be given by

$$\nu = \frac{2}{n\tau_1} \sinh \frac{v_a \tau}{kT},$$

where v_a is the activation volume.

By considering simplified geometrical situations, the preceding assumptions have lead the authors to the following expression for dislocation velocity in ice.

$$v_d = \frac{4}{9\pi} \frac{1}{\tau_0} \frac{b^4}{(r^*b)^{\frac{3}{2}}} \left(\frac{\tau}{G}\right)^{\frac{1}{2}} \exp\left(-\frac{1}{C}\right) \sinh \frac{(br^*)^{\frac{3}{2}}(G\tau)^{\frac{1}{2}}}{2kT}, \quad (2)$$

where b is the Burgers' vector, G the shear modulus, and $\tau_0 \approx 10^{-13}$ s; τ_0 can be identified either with the mean time for a molecule to be displaced with the velocity of sound within one molecular distance or to the reverse of the most probable frequency of translational modes of vibration as indicated by spectroscopy.

Equation (2) has been used to fit experimental results obtained by X-ray topography (Maï, 1976), taking properly into account the variation of v_d with stress, which is the more non-linear the higher the temperature.

New experimental results about dynamic behaviour of dislocations have been obtained in the case of HF-doped ice: on the one hand Maï and others (1978) have shown that HF induces a slight increase of the velocity of dislocations and moreover this velocity varies more rapidly with stress; on the other hand, the high-temperature internal friction of ice, which was interpreted in terms of movement of linear defects, is increased after HF doping and becomes more amplitude dependent (Vassoille and others, 1978).

The aim of this paper is to present an improvement of the preceding model in order to account for those recent experimental results on dislocation velocity of HF-doped ice single crystals.

In the first part, the most typical experimental results are presented: it is noteworthy that both techniques (direct X-ray topographic observations and internal-friction measurements) lead us to very analogous results. In the second part, a simplified analysis of the effect of the substitutional impurities is introduced. Finally, all the experimental results are discussed in the light of the whole model; the high-temperature internal friction is particularly considered.

2. EXPERIMENTAL RESULTS

2.1. *Experimental procedure*

Specimens in the form of bars of rectangular section (8 mm × 2 mm) are mechanically cut from a single-crystal block freshly grown by the Bridgman method. The diffusion coefficient of hydrogen fluoride in ice being very high (Fletcher, 1970, p. 137) this property is used for doping the specimens by covering them over with an HF solution. The HF concentration is estimated from the electrical resistivity of the melted specimen after measurement. Moreover, the displacement of the relaxation peak (Vassoille and others, 1977) confirms the result.

The rectangular bar is cut in two parts:

- (i) One part is about 20 mm long and is fixed on the goniometer of a Lang camera. Before each series of measurements of dislocation velocity, the crystallographic orientation of the specimen is determined and a topographic observation of the whole crystal is done. Then, a section of this crystal is chosen in order to observe the displacement of dislocations induced by a compressional stress applied by putting a load on the crystal. This displacement is measured by the double-images technique showing the position of the dislocations both before and after the application of the load. The whole Lang assembly is put in a box where the temperature is controlled between 250 and 272 K.
- (ii) The second part, about 80 mm long, is mounted in an inverted torsional pendulum. The variations of the logarithmic decay of oscillations with temperature is automatically provided (Etienne and others, 1975); the amplitude of oscillations is variable, thus measurements of internal friction as a function of strain amplitude are possible.

Hence, both measurements (dislocation velocity and internal friction) are made on the same material.

2.2. *Results on dislocation velocity*

Experimental points (Maï and others, 1978) shown in Figure 1(b) exhibit, in the case of HF doped ice, a non-linear relation between velocity and stress in the whole temperature range 251–270 K. It must be recalled (Maï, 1976) that with the same ice before doping, this non-linear relation is observed only above 260 K (Fig. 1(a)).

Furthermore HF induces an increase of the velocity of dislocations which is about twice that before doping.

2.3. *Results on internal friction*

When ice is doped with HF, the relaxation peak is observed at lower temperature than in case of pure ice (Fig. 2) indicating that the relaxation time is 70 times shorter. The HF content, which is supposed to be in substitutional solution, is then between 10 and 20 p.p.m. (Vassoille and others, 1977).

The high-temperature internal friction is clearly modified: it is increased (Fig. 2) and also it becomes more amplitude dependent (Fig. 3). Furthermore, the amplitude dependence appears at lower temperatures than in the case of pure ice.

It is noteworthy that the curves of Figure 3 are correlated with those of Figure 1; indeed, as the high-temperature internal friction is interpreted in terms of movement of linear defects, only a non-linear relation between velocity and stress can induce an amplitude-dependent internal friction.

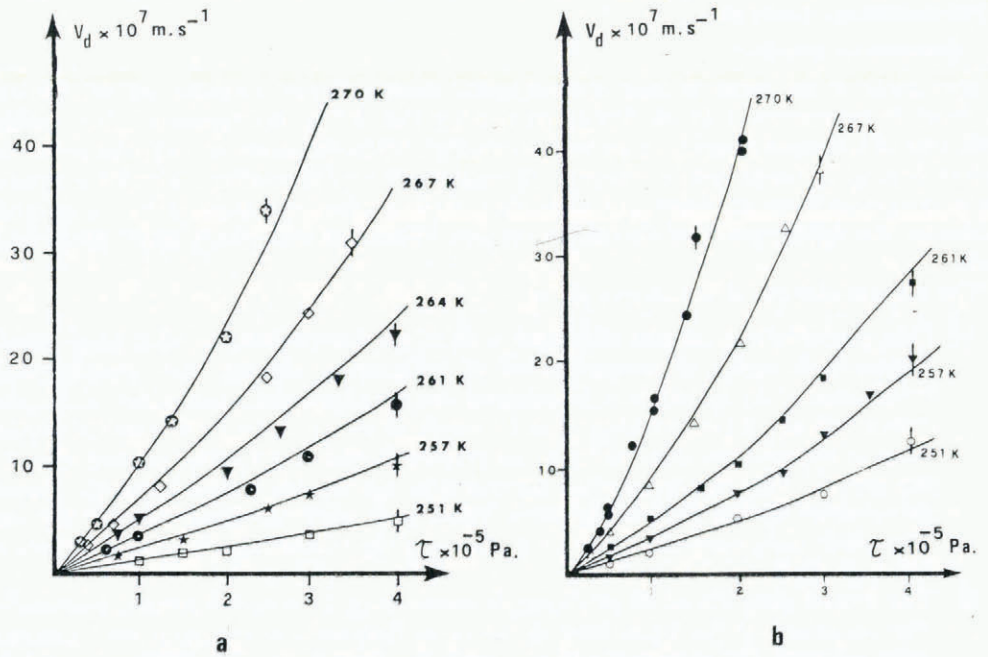


Fig. 1. Experimental points and theoretical curves giving the dislocation velocity in pure ice (a) and HF-doped ice (b).

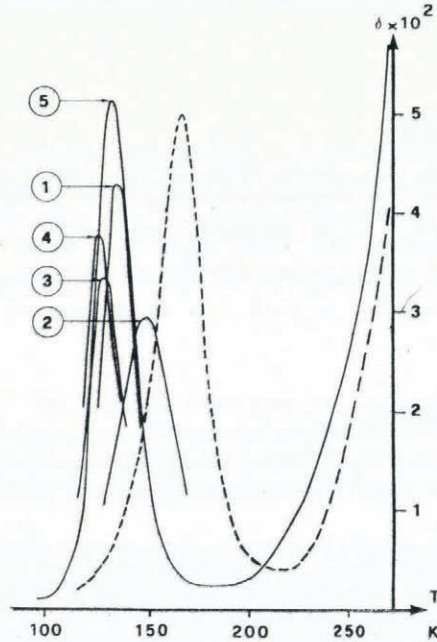


Fig. 2. Internal friction versus temperature before HF doping (dashed line) and after doping for five different specimens (curves 1 to 5).

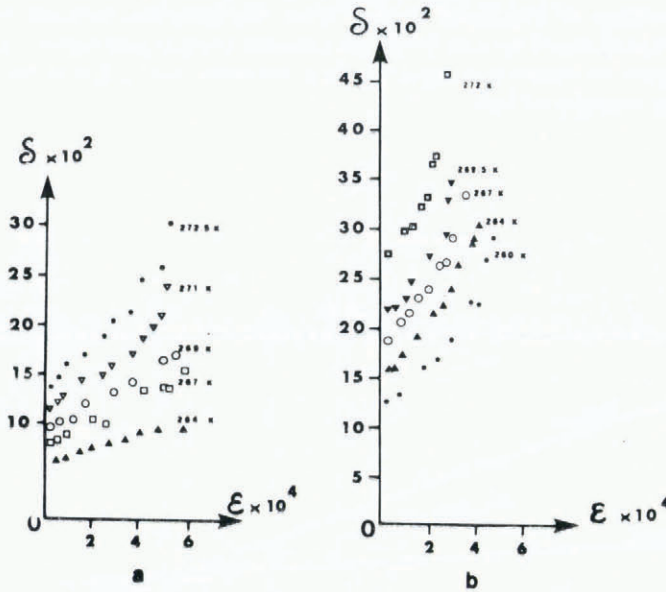


Fig. 3. Internal friction versus strain amplitude before (a) and after (b) HF doping.

3. DISCUSSION

3.1. Effect of a substitutional doping agent on dislocation velocity in ice

In an ice crystal we write $[I]_C$ for the molar fraction of a substitutional impurity and $[I]_{NC}$ for the molar fraction of the same impurity in the extended cores of dislocations. The chemical potential of this impurity has to have the same value in the two phases; hence

$$\frac{[I]_C}{[I]_{C \max}} = \frac{[I]_{NC}}{[I]_{NC \max}},$$

where $[I]_{C \max}$ and $[I]_{NC \max}$ are the maximum values of the impurity concentration in the crystalline and non-crystalline part respectively.

The partition coefficient is introduced as $K_S = [I]_{NC \max} / [I]_{C \max}$.

Therefore

$$[I]_{NC} = K_S [I]_C.$$

It is necessary to estimate a value of K_S in order to calculate the contribution $\Delta G(I)$, due to the impurity atoms, to the total variation of the free enthalpy induced by the extension of the dislocation core by one unit length in an ice crystal containing a concentration $[I]_C$ of dopant. $[I]_{C \max}$ can be obtained from the liquidus line of the equilibrium phase diagram of ice and impurity. $[I]_{NC \max}$ corresponds to the maximum value of the concentration when the core begins to melt; in fact, melting is only possible when there is an equilibrium between the increase in interfacial energy and the decrease in configurational energy. The approximation of linearized free-enthalpy-temperature curves is used once more and Figure 4 shows that this melting occurs at a temperature T in a material having a concentration of impurity $[I]_{NC \max}$; this temperature is between T_F and $T_{F'}$ ($T_{F'}$ being the temperature at which a bulk mixture of ice and impurity of the same composition would begin to melt), as indicated in Figure 4 and by the relation

$$2\pi r^*(I) \Delta\gamma = [(T_F - T) \Delta S_I + (T - T_{F'}) \Delta S_0] \pi r^*(I)^2, \tag{3}$$

where $\Delta\gamma$ is the increase of interfacial energy when the interface between crystal- and non-crystalline core is transformed into an interface between crystal and liquid, ΔS_0 is the melting entropy of the mixture of water and impurity (it is assumed that ΔS_0 is of the order of magnitude of the melting entropy of ice).

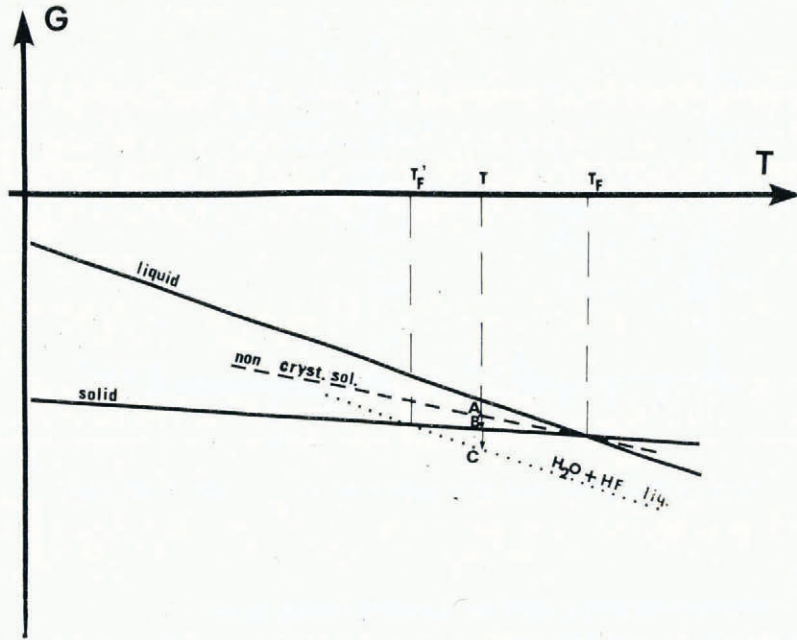


Fig. 4. Linearized approximation of the variation of the free enthalpy with temperature in the case of liquid water, ice, and non-crystalline core phase.

Equation (3) can be written

$$T_F - T_F' = \frac{2\Delta\gamma/r^*(I) + (T_F - T)(\Delta S_0 - \Delta S_1)}{\Delta S_0} \quad (4)$$

Then from the equilibrium phase diagram, it is easy to obtain $[I]_{NC \max}$ corresponding to each value of $(T_F - T_F')$ determined as a function of the temperature T using Equation (4).

At this stage an attempt can be made to apply this result to the case of ice doped with HF. In Figure 5, the liquidus line is shown and the solidus line is drawn with the points which correspond to a maximum content of HF in ice as determined by Haltenorth and Klinger (1977). (It has been assumed that HF forms mainly a substitutional solution.) In the range 240–270 K, the values of $[HF]_{C \max}$, $[HF]_{NC \max}$ and K_S are calculated from data in Figure 5 and Equation (4); these values are given in Table I.

It will be noticed that such values cannot be obtained without $r^*(HF)$ being known. However, an attempt will be made to calculate approximate values for $(T_F - T_F')$; since experimental data on HF-doped ice show that the relation between the dislocation velocity and the stress on the one hand is less linear in the whole temperature range 250–270 K (i.e. $r^*(HF) > r^*$) and, on the other hand, exhibits only a small variation with temperature (i.e. the decrease of $r^*(HF)$ with temperature is less than that of r^*), for every temperature a value $r_0^*(HF)$ has been used in Equation (4) which is the average between $r^*(T)$ and $r^*(273)$. (The theoretical curve $r^*(T)$ which is chosen is that leading to the interpretation of experimental data, as will be mentioned later.)

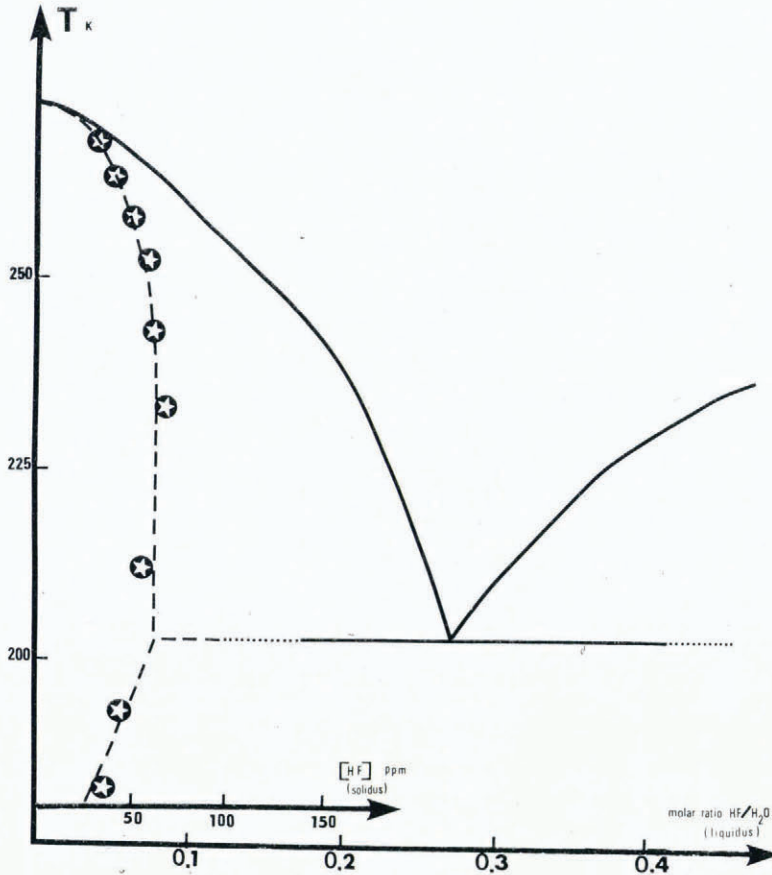


Fig. 5. Phase diagram HF-H₂O; experimental points are given by Hallenorth and Klinger (1977).

TABLE I. VALUES OF PARAMETERS FOR HF-DOPED ICE

T_K	$r_0^*(\text{HF})$ 10^{-10} m	$(T_F - T'_F)_K$	$[\text{HF}]_{\text{NC max}}$	$[\text{HF}]_{\text{C max}}$ 10^{-6}	K_S
270	13	34.7	0.195	25	7 800
260	11	44.4	0.225	44	5 100
250	10.5	49.9	0.237	55	4 300
240	10	55.6	0.248	60	4 100

The results presented in Table I indicate a strong accumulation effect of HF molecules in the dislocation cores: this conclusion is in agreement with the hypothesis of Hallenorth and Klinger (1977), nevertheless, the whole quantity of HF molecules being in the cores of the dislocations (maximum density: 10^{10} m^{-2}) proved to be about three orders of magnitude less than the total content of HF in the crystal, which is self-consistent with our preceding assumption indicating that HF would mainly be found in substitutional solution.

Furthermore, K_S seems to increase slightly with temperature, especially in the vicinity of T_F ; since the thermodynamic approach which was introduced to describe the melting of mixture ice-impurity is probably not precise enough, this K_S variation will not be taken into account and an average value of $K_S \approx 5 \times 10^3$ will be used.

The accumulation of HF molecules in the dislocations cores induces an additional variation of the free enthalpy $\Delta G(\text{HF})$ which is given by

$$\Delta G(\text{HF}) = -\pi r^2 (\Delta H_{\text{HF}} - T \Delta S_{\text{HF}}) K_{\text{S}}[\text{HF}]_{\text{C}}.$$

Once more, only the upper limit of the parameter ΔH_{HF} is known: it is the enthalpy of dissolution of HF in water ($3 \times 10^9 \text{ J m}^{-3}$) taken from an infinite dilution until a concentration of about 0.1 is reached; the other parameter, ΔS_{HF} , is approximately the entropy of mixing HF molecules (concentration $K_{\text{S}}[\text{HF}]_{\text{C}}$) with H_2O molecules in the dislocations cores (about $10^6 \text{ J m}^{-3} \text{ K}^{-1}$).

In this case the relation giving ΔG (Perez and others, 1978) must be modified to take into account $\Delta G(\text{HF})$; thus $r^*(\text{HF})$ can be calculated in the case of an ice crystal doped with HF (with global concentration $[\text{HF}]_{\text{C}}$) from the relation

$$r^*(\text{HF}) = \frac{-\frac{1}{2}\gamma_1 + \{(\frac{1}{2}\gamma_1)^2 + \beta G b^2 / 2\pi [\Delta S_1 \Delta T - (\Delta H_{\text{HF}} - T \Delta S_{\text{HF}}) K_{\text{S}}[\text{HF}]_{\text{C}}]\}^{\frac{1}{2}}}{\Delta S_1 \Delta T - (\Delta H_{\text{HF}} - T \Delta S_{\text{HF}}) K_{\text{S}}[\text{HF}]_{\text{C}}}. \quad (5)$$

Theoretical curves of $r^*(\text{HF})$ as a function of temperature corresponding to $[\text{HF}]_{\text{C}} = 10^{-5}$ and to several values of the parameters ΔH_{HF} and ΔS_{HF} , are shown in Figure 6. It appears clearly that doping ice with HF induces an increase of r^* which is, moreover, less dependent on temperature, in agreement with the preceding remarks about the experimental data.

For better accuracy, it would be necessary to use the values of $r^*(\text{HF})$ instead of $r_0^*(\text{HF})$ in Table I and to recalculate as implied by iterative methods. Nevertheless, this proved to be

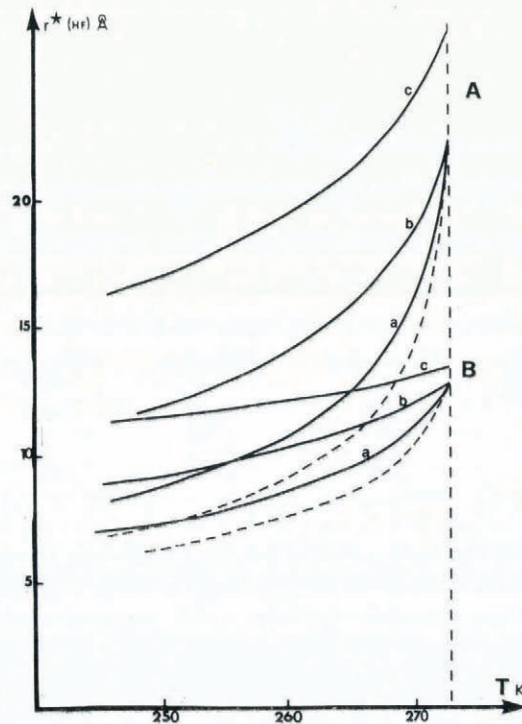
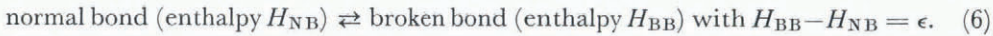


Fig. 6. Theoretical values of $r^*(\text{HF})$ versus temperature with $[\text{HF}]_{\text{C}} = 10^{-5}$; $K_{\text{S}} = 5 \times 10^3$; $\Delta S_1 = 5 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$; $\gamma_1 = 4 \times 10^{-3} \text{ J m}^{-2}$ (A) or $7 \times 10^{-3} \text{ J m}^{-2}$ (B); $\Delta H_{\text{HF}} = 10^9$ (a), 2×10^9 (b), 2.5×10^9 (c) J m^{-3} ; and $\Delta S_{\text{HF}} = 3.66 \times 10^6$ (a), 7.33×10^6 (b), 9.14×10^6 (c) $\text{J m}^{-3} \text{ K}^{-1}$. Dashed lines: $[\text{HF}]_{\text{C}} = 0$.

unnecessary since the substitution of $r_0^*(\text{HF})$ by $r^*(\text{HF})$ leads to a variation in K_s which is small with regard to the approximation implied by taking K_s constant and equal to 5×10^3 .

Not only do the HF molecules modify the radius of dislocation cores, but also the structure relaxation time τ_1 calculated in the preceding part of this work (Equation (1)). In fact, the concentration of broken bonds C in the dislocations cores is probably modified by the presence of the HF molecules and becomes C' . Due to thermal activation, the hydrogen bonds whose energy is situated between ϵ and $\epsilon + d\epsilon$ exhibit the following equilibrium:



Following both this equilibrium and the linear distribution law it was assumed that the number of intrinsic broken bonds L_B among those considered is given by:

$$L_B = \frac{4N_0\epsilon d\epsilon}{E^2[1 + \exp(\epsilon/kT)]}.$$

The HF molecules can form only one hydrogen bond instead of two in the case of H_2O molecules; thus, to have the bond AB (Fig. 7a) broken, two conditions are required, first the H_2O molecule A can be replaced by one HF molecule (the probability is $K_s[\text{HF}]_C$), and secondly the proton of HF is placed in position 2 (the probability is $\frac{1}{2}$). Hence the number of extrinsic broken bonds can be expressed by

$$L_B(\text{HF}) = \frac{2N_0}{E^2} K_s[\text{HF}]_C \epsilon d\epsilon.$$

In fact, there is a modification of the equilibrium (6) when impurity molecules such as HF are added and the number of broken bonds is L_B' . The analysis of this modification of

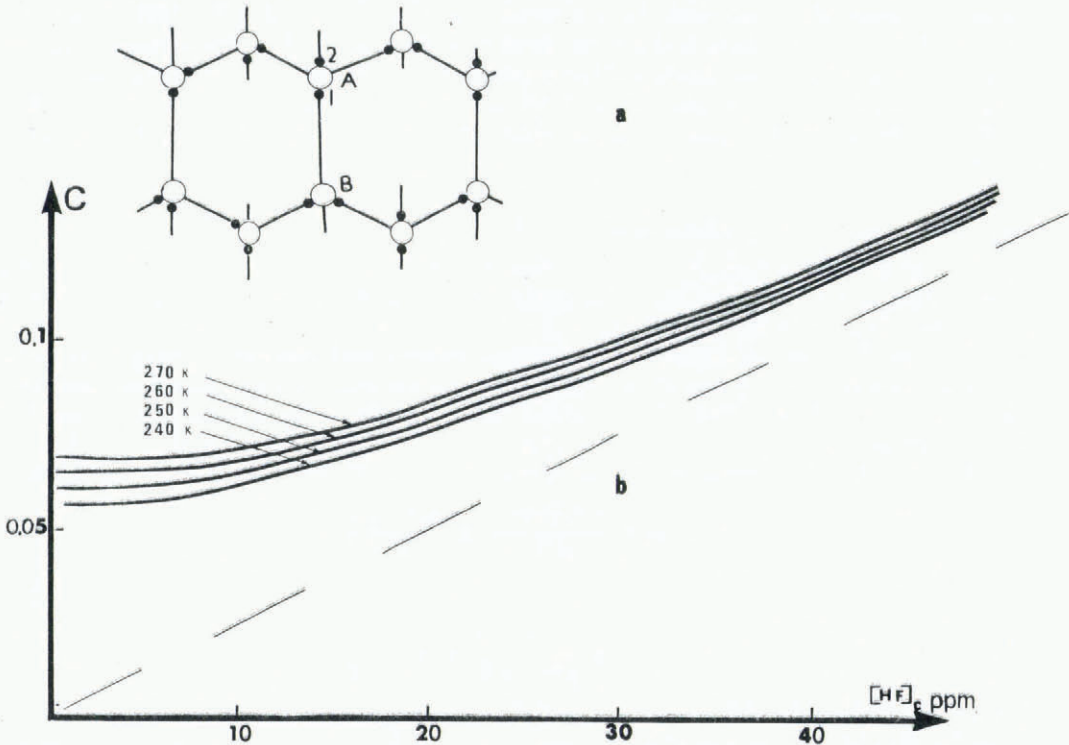


Fig. 7. Concentration of broken bonds such as AB as discussed in the text (a) as a function of $[\text{HF}]_C$ for several temperatures (b).

equilibrium is similar to that of Kröger (1974) concerning the effect of HF on the concentration of ionic or Bjerrum defects in ice; this analysis being complicated, two extreme cases will be discussed:

- (i) $L_B(\text{HF}) \ll L_B$: the number of broken bonds L_B' is approximately L_B ,
- (ii) $L_B(\text{HF}) \gg L_B$: L_B' is approximately $L_B(\text{HF})$.

The limit between those two cases is given by

$$L_B = L_B(\text{HF}),$$

which corresponds to a critical value of ϵ given by:

$$\epsilon_0 = kT \ln \left[\frac{2}{K_S[\text{HF}]_C} - 1 \right].$$

Then the total number of broken bonds can be calculated

$$\Sigma L_B' = \int_0^{\epsilon_0} L_B + \int_{\epsilon_0}^E L_B(\text{HF}).$$

The concentration of broken bonds is:

$$C' = \frac{\Sigma L_B'}{2N_0} = \frac{1}{2} K_S[\text{HF}]_C \left[1 - \left(\frac{\epsilon_0}{E} \right)^2 \right] + \frac{2}{E^2} \int_0^{\epsilon_0} \frac{\epsilon \, d\epsilon}{1 + \exp(\epsilon/kT)}.$$

This result is in agreement with the fact that when $[\text{HF}]_C$ is high, C' is equal to $\frac{1}{2} K_S[\text{HF}]_C$, which corresponds to extrinsic broken bonds only ($\epsilon_0 \approx 0$) and when $[\text{HF}]_C$ is small, C' approaches the concentration of intrinsic broken bonds C ($\epsilon_0 \approx E$). The variation of C' versus $[\text{HF}]_C$ is numerically calculated and the result is shown in Figure 7b in the case of a temperature ranging between 240 and 270 K. Such a result will be used and the velocity of dislocations will be given by Equation (2) in which r^* and C are replaced by $r^*(\text{HF})$ and C' respectively.

3.2. Application to velocity measurements

In our previous paper, it was shown how Equation (2) could be used in the case of pure ice. Owing to the improvement of the theory, it is possible now to explain the results in both the cases of pure and HF-doped ice.

Though Equation (2) is difficult to compare directly with the experimental data since the physical factors C (or C') and r^* (or $r^*(\text{HF})$) are not known, the latter depending on ΔS_1 and γ_1 (and ΔH_{HF} , ΔS_{HF}), the effect of shear stress appears to be correctly described by the present analysis.

In fact, at low temperature (i.e. with low values of r^*) and (or) at very low shear stress

$$\sinh \frac{(br^*)^{\frac{1}{2}}(G\tau)^{\frac{1}{2}}}{2kT} \approx \frac{(br^*)^{\frac{1}{2}}(G\tau)^{\frac{1}{2}}}{2kT}.$$

Then we have

$$v_d \approx \frac{2}{9\pi} \frac{1}{\tau_0} \frac{\tau b^4}{kT} \exp\left(-\frac{1}{C}\right), \quad (7)$$

thus v_d varies linearly with the stress τ , and this linear dependence disappears when τ increases and the non-linearity is the more pronounced the higher the temperature or the higher the HF content. This remark is in very good agreement with experimental data.

Equation (7) has been used to obtain E from the temperature dependence of the slope at zero stress of the curves $v_d(\tau)$, within a temperature range included between 251 and 270 K (Fig. 8(a)). The values $0.10 \text{ eV} < E < 0.11 \text{ eV}$ was obtained. Thus the value $E = 0.105 \text{ eV}$ was used to draw the theoretical curves of v_d against τ and T .

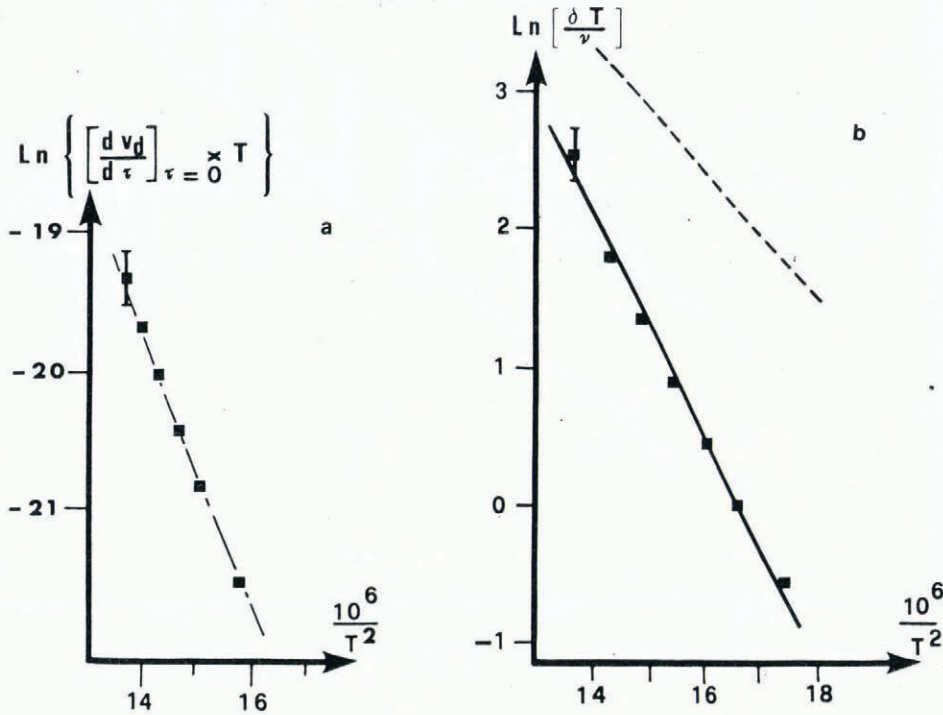


Fig. 8. Comparison between plots of either logarithm of the slope at zero stress of dislocation velocity (a) or logarithm of low stress internal friction (b) (solid line: pure ice; dashed line: doped ice).

In the case of HF-doped ice, Equation (7) is still valid with C replaced by C' , so it is possible to obtain C' from low-stress values of the velocity of dislocations measured in HF-doped ice (concentration $\approx 10^{-5}$). Figure 9 shows that the values of C' are slightly higher than C (in both cases the calculation is done with $\tau_0 = 10^{-13} \text{ s}$ and $b = 4.5 \times 10^{-10} \text{ m}$). Moreover the calculated points are in agreement with the theoretical curve plotted using results from Figure 7: thus the analysis of the preceding section does take into account the effect of HF, which induces an increase of the velocity by a factor ≈ 2 .

In the range of non-linear behaviour, other factors (γ_1 , ΔS_1 , ΔH_{HF} , and ΔS_{HF}) should be defined from the stress dependence of v_d and from the variation of this stress dependence with temperature. In the present work the values r^* and $r^*(\text{HF})$ are obtained from the results of Mai; these results are shown in Figure 10.

In the case of pure ice, a satisfactory agreement between experimental points and the theoretical curve is obtained by using $\gamma_1 = (5 \pm 1) \times 10^{-3} \text{ J m}^{-2}$ and $\Delta S_1 = (5 \pm 1) \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$. In the case of HF-doped ice, two simplifying assumptions are made:

- (i) The parameters γ_1 and ΔS_1 are nearly the same as with pure ice.
- (ii) As suggested by the variation of experimental values of r^* and of $r^*(\text{HF})$ with temperature (Fig. 10) the effect of the doping agent is negligible near the melting point T_F of ice, that is $\Delta H_{\text{HF}} - T_F \Delta S_{\text{HF}} \approx 0$.

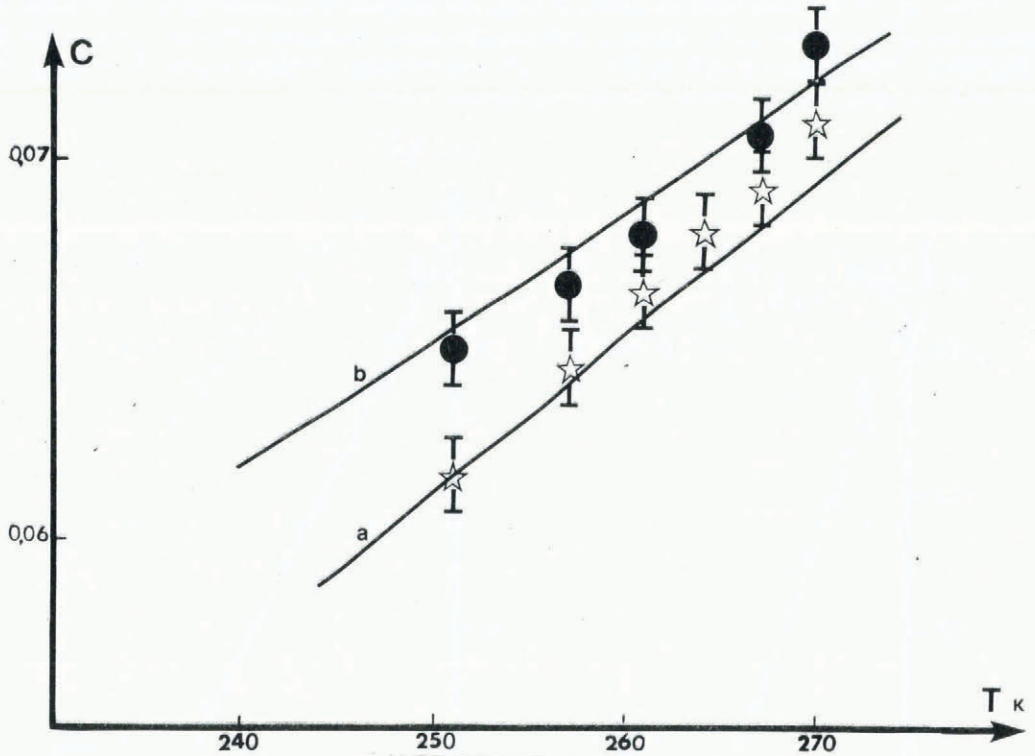


Fig. 9. Concentration C as function of temperature; experimental points obtained from the slope of curves $v_d(\tau)$ at $\tau = 0$ and theoretical curves obtained with $E = 0.105$ eV in the case of pure ice (a) or with data of Figure 7 in the case of doped ice (b).

In these conditions, a reasonable agreement between experimental and the theoretical curves (b) (Fig. 10) is obtained by putting $\Delta H_{HF} = (1.2 \pm 0.2) \times 10^9$ J m $^{-3}$ and $\Delta S_{HF} = (4.4 \pm 0.7) \times 10^6$ J m $^{-3}$ K $^{-1}$ in Equation (5).

Thus, these values of E (or G), and r^* on the one hand, and C' and $r^*(HF)$ on the other have been used in Equation (2) to draw theoretical curves of $v_d = F(\tau, T)$ for pure and doped ice respectively. Figure 1(a) and (b) shows a comparison between the theoretical curves and Maï's experimental results.

It is noteworthy that ΔS_I and γ_I are, as predicted, lower than the entropy of melting ice (1.1×10^6 J m $^{-3}$ K $^{-1}$) and the ice-liquid-water interfacial energy (3×10^{-2} m $^{-2}$) respectively; similarly, ΔH_{HF} and ΔS_{HF} are of the same order as the enthalpy of dissolution of HF in water (3×10^9 J m $^{-3}$) and the entropy of mixing HF molecules with H $_2$ O molecules (about 10^6 J m $^{-3}$ K $^{-1}$) respectively.

3.3. Application to internal friction results

Since the high-temperature internal friction has been interpreted in terms of movement of dislocations, any description of this internal friction must imply the use of a relation between dislocation velocity and stress.

Indeed, the strain-rate of a crystal having a dislocation density ρ_d is

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

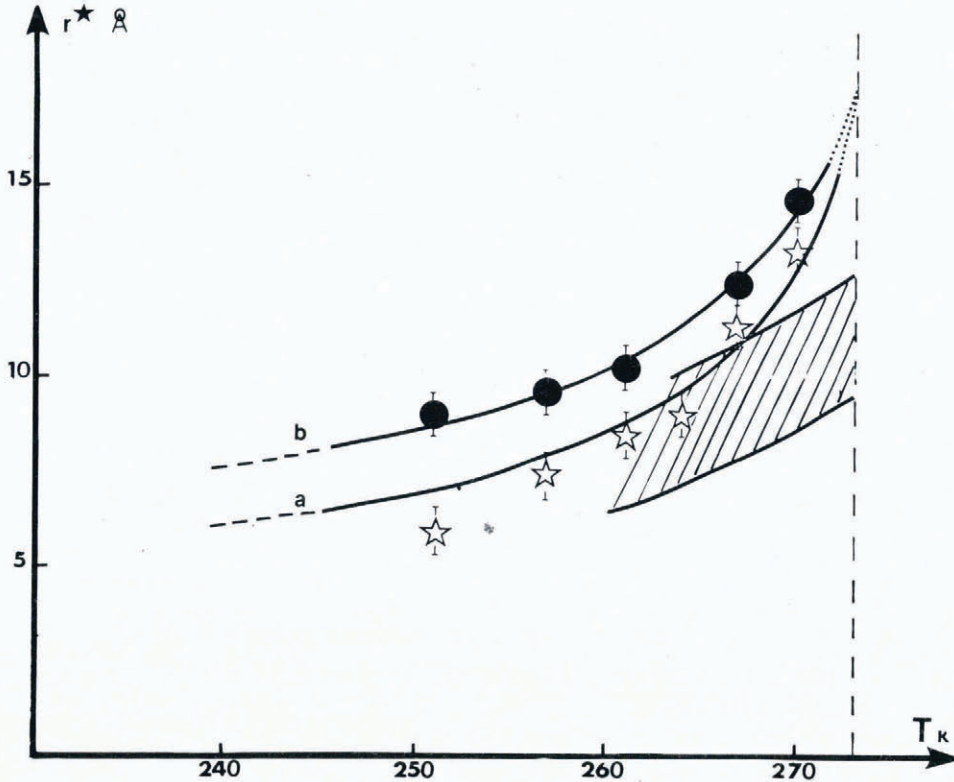


Fig. 10. Variation of r^* with temperature; experimental points correspond to X-ray observations in the case of pure ice (a) and of HF-doped ice (b). Theoretical curves are calculated with $\gamma_i = 5 \times 10^{-3} \text{ J m}^{-2}$, $\Delta S_1 = 5 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$, $\Delta H_{\text{HF}} = 1.2 \times 10^9 \text{ J m}^{-3}$, and $S_{\text{HF}} = 4.4 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$. All the results obtained by internal friction measurements done on six different specimens of pure ice are in the hatched band.

The logarithmic decrement is given by

$$\delta = \frac{1}{2} \frac{\Delta W}{W},$$

where $\Delta W = \oint \tau d\epsilon$ is the energy dissipated during one cycle of sinusoidal stress, and

$W = \frac{\tau_m^2}{2G}$ is that maximum elastic energy during this stress cycle.

If the sine stress is given by $\tau = \tau_m \sin 2\pi\nu t$ we obtain:

$$\delta = \frac{G\rho ab}{\tau_m} \oint \sin 2\pi\nu t v_d dt. \quad (8)$$

As a first step, it was proposed (Perez and others, 1976) that:

- (i) kink diffusion induces amplitude-independent internal friction;
- (ii) thermal activation of double kinks induces temperature and amplitude-dependent internal friction.

Actually, the result obtained at high-amplitude stresses or after HF doping have shown that this description is not in good agreement with all the experimental data.

Another attempt (Perez and others, 1978) was made by replacing v_d in Equation (9) by an empirical expression in agreement with results recalled in Figure 1.

In fact, it is now possible to calculate Equation (8) by using Equation (2); after some simplification we get

$$\delta = \delta(0, T) \frac{\sinh \alpha \tau_m^{\frac{1}{2}}}{\alpha \tau_m^{\frac{1}{2}}}, \quad (9)$$

where

$$\left. \begin{aligned} \alpha &= \frac{(br^*)^{\frac{2}{3}} G^{\frac{1}{2}}}{2kT}, \\ \delta(0, T) &= \frac{Kb^5 \rho_d}{9\pi kTP\tau_0} \exp\left(-\frac{1}{C}\right), \end{aligned} \right\} \quad (10)$$

P is the period of the pendulum, and $K = GP^2 \approx 3 \times 10^9 \text{ N m}^{-2} \text{ s}^2$.

At low stress, Equation (9) can be simplified and we have

$$\delta = \delta(0, T). \quad (11)$$

Thus it can be concluded that though there is only one type of internal friction due to the movement of dislocations in ice, this can be observed either at low stress where it is only temperature dependent (Fig. 2) or at increasing stresses where it becomes amplitude dependent above a stress which is lower the higher the temperature.

3.3.1. Interpretation of amplitude-dependent internal friction

First, local internal friction must be calculated from global results shown in Figure 3 which correspond to a specimen with a stress gradient (Perez and others, 1965).

Then it has been verified that it is possible to find values of α such that straight lines are obtained when plotting $\delta \alpha \tau_m^{\frac{1}{2}}$ against $\sinh \alpha \tau_m^{\frac{1}{2}}$ (Fig. 11a and 11b for pure and HF-doped ice respectively). r^* is calculated with regard to Equation (10). All the values of r^* versus temperature obtained for six different specimens of pure ice are in the hatched band in Figure 10.

In addition, the comparison between an HF-doped ice and the same ice before doping is shown in Figure 12. Despite the lack of accuracy, it can be noticed that HF doping induces an increase of r^* which becomes less temperature dependent: these results are comparable to those obtained from X-ray topography (Fig. 10) and are in agreement with the preceding model.

3.3.2. Temperature-dependent internal friction measured at low stresses

Equations (10) and (11) have been used to describe the low-stress temperature-dependent internal friction. In the case of pure ice where C is proportional to T^2 , a straight line is obtained when $\ln(\delta(0, T) T/\nu)$ is plotted as a function of T^{-2} (Fig. 8b). On the one hand, the slope gives E as $(0.095 \pm 0.005) \text{ eV}$ and, on the other hand, the ordinate extrapolated to infinite temperature gives the density of dislocations $5 \times 10^7 < \rho_d < 5 \times 10^8 \text{ m}^{-2}$. It is noteworthy that these values are in agreement with those obtained from topographic observations $(0.105 \pm 0.005) \text{ eV}$ and $10^{8 \pm 1} \text{ m}^{-2}$ respectively.

The situation is more complicated with doped ice; C' is given by (Section 3.1)

$$C' \approx C_1(kT/E)^2 + C_2,$$

with C_1 and C_2 constants depending on doping concentration. This explains why the slope of

the straight line obtained in the diagram $\ln(\delta(o, T) T)/\nu$ against T^{-2} is lower (Fig. 8b) after doping ice with HF. More generally, it appears that the present analysis of low-stress temperature-dependent internal friction is easily applicable only in the case of ice of high purity with fresh dislocations (freshly grown ice crystal or plastically deformed ice). With ice containing some impurities or with aged ice, the slope of the line $\ln(\delta(o, T) T)/\nu = f(T^{-2})$ is always lower.

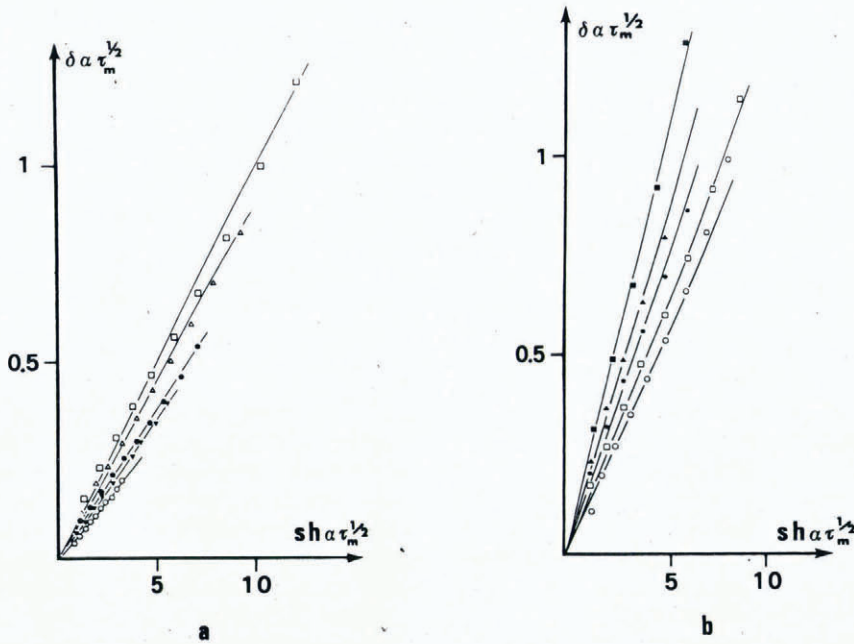


Fig. 11. Representation of the experimental data of Figure 3 in the diagram $\delta \alpha \tau_m^{1/2}$, $\sinh \alpha \tau_m^{1/2}$ in the case of pure ice (a) or doped ice (b).

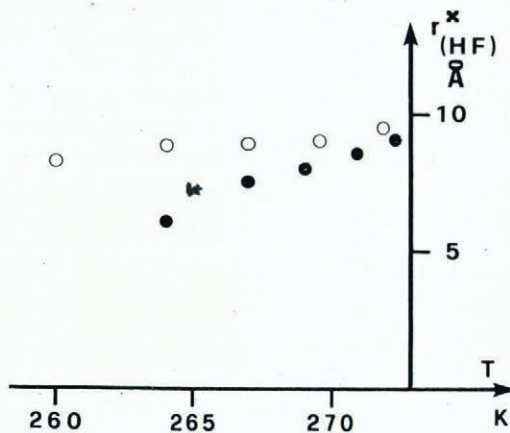


Fig. 12. Variation of r^* obtained from internal friction measurements done on the same specimen before (black dots) and after (white dots) doping.

4. CONCLUSION

In short the following remarks can be drawn out:

(a) The present model provides the possibility of calculating, for the velocity v_d of dislocations in ice, theoretical values which agree with experimental results, contrary to previous models. Moreover the non-linear relation between v_d and the stress is thus properly described.

(b) It is shown that doping ice with about 10 p.p.m. of HF induces a slight increase of C (concentration of broken bonds) leading to an increase of v_d by a factor ranging from 1 to 10; experiments yield a factor which approximates 2; it will be remembered that the relations obtained from assuming the reorientation of the H_2O molecules indicates, for the same doping, a factor of 10 to 100 depending on purity of non-doped ice. This appears to be another argument against the description of obstacles to dislocation glide in ice in the form of proton disorder. It is noteworthy that if HF induces a softening effect in ice, NH_3 leads rather to a hardening effect as shown by Jones and Glen (1969) on an ice single crystal doped with 5 p.p.m. NH_3 , though it was not observed in the case of ice with only 0.6 p.p.m. NH_4OH (Nakamura and Jones, 1973). This hardening effect can be explained by the preceding analysis: the equilibrium reaction (6) is displaced towards the left side by NH_3 molecules if the existence of an accumulation of such molecules in the core is once more admitted. Thus the concentration C of broken bonds is decreased and v_d is expected to decrease.

(c) When the temperature is not high enough (typically less than 200 to 250 K), the preceding assumption concerning the extended core is probably no longer valid. In these conditions the crystalline core aspect seems more probable since it allows obstacles to dislocation glide which were anticipated (proton disorder, Peierls hills, . . .) to be considered. This last remark may explain that the softening effect of HF at 253 K is small compared with the effects observed at 203 K (Jones and Glen, 1969). Experimental data in an extended temperature range are needed in order either to improve the model or to test the applicability of the models quoted previously (Whitworth, 1978).

(d) Such a description of the dynamic behaviour of dislocations has been applied to interpret the high-temperature internal friction of ice measured at low frequency. Theoretical expressions have been obtained which are in a fair agreement with experimental features observed in the case of pure or HF-doped ice.

To sum up, a model of a dislocation with a non-crystalline extended core added to the assumption of correlated movements of H_2O molecules seems, at present, the only model able to take into account all the experimental features of dynamic behaviour of dislocations in ice. When the ice is HF-doped, the radius of the extended core is increased and becomes less temperature dependent; moreover, the rate of transition from one configuration to another by correlated movements of H_2O molecules is higher, leading to a small increase of dislocation velocity. These characteristics have lead us to interpret in a self-consistent way both types of results obtained either by direct X-ray measurements of the velocity of dislocations or by internal friction measurements at low frequency.

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