COOPERATIVE MOVEMENT OF H₂O MOLECULES AND DYNAMIC BEHAVIOUR OF DISLOCATIONS IN ICE Ih

By J. PEREZ, C. MAÏ and R. VASSOILLE

(Groupe d'Études de Métallurgie Physique et de Physique des Matériaux, Institut National des Sciences Appliquées de Lyon, E.R.A. no. 463, Bâtiment 502, 20, avenue A. Einstein, F-69621 Villeurbanne-cedex, France)

ABSTRACT. A new model of dislocations glide in ice Ih is proposed. In developing this model certain assumptions are made: (i) dislocations have a non-crystalline extended core, and (ii) transitions occur through cooperative movements of H₂O molecules in the 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 results are in agreement with experimental data.

RÉSUMÉ. *Mouvement coopératif des molécules H₂O et comportement dynamique des dislocations dans la glace Ih.* Un nouveau modèle de glissement des dislocations dans la glace Ih est développé à partir des deux hypothèses suivantes: (i) les dislocations présentent un coeur étendu de matière non cristalline, et (ii) des transitions entre différentes configurations se produisent grâce à des mouvements coopératifs de molécules d'eau. Nous obtenons une relation entre la vitesse v_d des dislocations la contrainte τ et la température T; 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 est bien en accord avec les résultats portant sur les mesures directes de v_d.

ZUSAMMENFASSUNG. *Kooperative Bewegung von H₂O-Molekülen und dynamisches Verhalten von Versetzungen in Eis Ih.* Ein neues Modell der Versetzungsgleitung in Eis Ih wird vorgeschlagen. Dieses Modell wird entwickelt unter der Annahme, dass (i) Versetzungen einen ausgedehnten nicht-kristallinen Kern besitzen und (ii) Übergänge durch kooperative Bewegung von H₂O-Molekülen im Versetzungskern erfolgen. Man erhält eine Beziehung zwischen der Geschwindigkeit v_d der linearen Fehlstellen und der Schubspannung τ oder der Temperatur T. Diese Beziehung zeigt, dass sich v_d linear mit τ ändert bei niedrigen Werten von τ und (oder) T, aber dass es sich bei hohen Spannungen stärker ändert. Diese Nichtlinearität ist umso bedeutender, je höher die Temperatur ist. Diese Ergebnisse stimmen mit experimentellen Werten überein.

INTRODUCTION

Attempts were made several years ago to measure the dislocation velocity in ice Ih; it has been shown that its value, which depends on temperature and on stress, is as low as 10^{-8} to 10^{-5} m s^{-1}. The nature of obstacles to dislocation glide has to be identified. It has been proposed by Glen (1968) that the disorder of the protons on the O–H–O bonds in ice can be such an obstacle.

Glen's hypothesis has been quantitatively improved by Perez and others (1975), Whitworth and others (1976) and Frost and others (1976). In all cases, assuming a kink model, the following relation was found for dislocation velocity:

$$v_d = \alpha \mathcal{N}_k \frac{b^5 \tau}{k T \tau_r},\qquad (1)$$

where τ is the shear stress, b the Burgers vector, $\mathcal{N}_k$ the concentration of kinks along the dislocation, and α is a numerical factor equal to 8 following rough approximations (on average one bond in two is mismatched (Perez and others, 1975)); after a more convincing statistical analysis of the mismatched bonds α has been found to be equal either to 2.6 (Frost and others, 1976) or to 2.25 (Bjerrum defects) and 1.1 (ionic defects) (Whitworth and others, 1976). The major difficulty is to define the relaxation time τ_r: on the one hand, if a theoretical value is calculated according to microscopic quantities such as frequency factor, activation energy of formation, and migration of defects, which are only known with a non-negligible uncertainty, the value $1 < v_d/b < 10^3$ s^{-1} is obtained (Perez and others, 1975). On the other hand, if τ_r is directly related to the dielectric relaxation time, the value $v_d/b \leqslant 50$ s^{-1}

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is obtained (Whitworth and others, 1976) showing a discrepancy with the experimental value which is, for the same conditions ($T = 255$ K and $\tau = 10^5$ N m^{-2}), $200 < v_\mathrm{d}/b < 900$ s^{-1} (Perez and others, 1975; Maï, 1976).

Furthermore, new experimental results obtained by Maï (1976) from X-ray topographic observations have shown that the velocity of dislocations is not proportional to τ as indicated by Equation (1) but varies more rapidly; in fact the variation is more rapid with stress the higher the temperature.

The criticism of the models describing the movement of dislocations in ice through different obstacles (mismatched bonds without or with ionic defects in the dislocation core, Peierls hills, self diffusion, climbing jogs, anelastic loss (Weertman, 1963), etc.), has led to the conclusion that none of these models are able to explain all the experimental features. However, Goodman and others (1977) have shown that plastic deformation of ice is obtained through different physical processes and they differentiated diffusional mechanisms (Herring–Nabarro or Coble creep, climbing dislocations, etc.) from a gliding mechanism which is probably the major mechanism at high stress ($10^{-4} < \tau/G < 10^{-2}$, where G is the shear modulus).

In the present work a new model for the description of dislocation glide in ice Ih is proposed which is in better agreement with experimental data.

In the first part, the hypothesis about the non-crystalline structure of dislocation cores in ice is introduced; in the second part, a simplified description of cooperative movements of H$_2$O molecules in these non-crystalline dislocations cores is proposed; this description is used, in the third part, to develop a model for dislocation movement under an applied stress and due to thermal energy fluctuations. In the last part, this model is discussed in the light of experimental data, including doping effects.

Structure of dislocation cores in ice Ih

Generally, the exact structure of dislocation cores is not known; in the case of ice, two suggestions were introduced:

(i) Dislocations might be dissociated following the reaction (Maï and others, 1977):

$$\frac{a}{3}[11\bar{2}0] \rightarrow \frac{a}{3}[10\bar{1}0] + \frac{a}{3}[01\bar{1}0].$$

The width of dissociation depends on the stacking-fault energy. The value of this energy is not known but is probably lower than that of grain boundaries, hence the width of dissociation would be greater than b.

(ii) Dislocation cores might have a liquid structure, and then the elastic energy of dislocations would be lowered; the dimension of the cores is limited due to the energy of the liquid–solid interface. But this dimension is of the order of b (Nye, 1973), which is too small to give any physical meaning to such an assumption.

Furthermore, in solids with directed bonds, the dislocation energy in the core is probably higher since there are either broken bonds or highly distorted bonds. This statement is supported in the case of ice (Yosida and Wakahama, 1962) by the proposed model of balls showing dangling bonds along edge dislocations and distorted bonds along screw dislocations; a similar description was given in the case of covalent solids of the diamond structure by Hornstra (1958). Actually, a decrease of the free energy of the crystal containing linear defects is expected when there is a rearrangement of molecules or atoms in dislocation cores causing the disappearance (edge dislocations) or the appearance (screw dislocations) of some dangling bonds (Hornstra, 1958; van Bueren, 1960, p. 599).

These three remarks lead us to the more general assumption, that the free energy of an ice crystal containing a dislocation of unit length can be lowered by a value of ΔG if a non-crystalline arrangement of H$_2$O molecules can exist around the dislocation line, resulting in

core energy and elastic energy being suppressed; the dimensions of this non-crystalline molecular arrangement are then limited by the increase of entropy of configuration and by the energy of the interface between crystalline and non-crystalline domains.

As a first attempt, the problem can be simplified by considering that the form of the non-crystalline molecular arrangement (hereafter called "extended core") is a circular cylinder.

Thus, we have, per unit length of dislocation,

$$\Delta G = -E_c - \beta G b^2 \ln \frac{r}{r_0} + 2\pi r \gamma_1 + \pi r^2 \Delta S_1 \Delta T. \qquad (2)$$

The first term corresponds to the energy of the non-extended core (radius r_0); the second term is the elastic energy of the dislocation in a cylinder of radius r; the constant β is given by

$$\beta = \frac{1 - \nu \, \cos^2\theta}{4(1 - \nu)},$$

where ν is Poisson's ratio and θ the angle between the dislocation line and its Burgers vector.

The two other terms correspond to an increase of interfacial energy and configurational energy (in the approximation of linearized free-enthalpy–temperature curves) respectively, when the core is extended over a cylinder of radius r (γ_1 is the energy per unit area of interface between crystalline and non-crystalline domains, ΔS_1 the variation of entropy per unit volume of material transforming from crystalline to non-crystalline state, and $\Delta T = T_F - T$, T_F being considered as equal to the melting temperature of ice).

The extension of the core is thermodynamically possible if the free energy can be lowered ($\Delta G < 0$); consequently this extension is obtained when $r = r^\star$, which corresponds to the equilibrium condition:
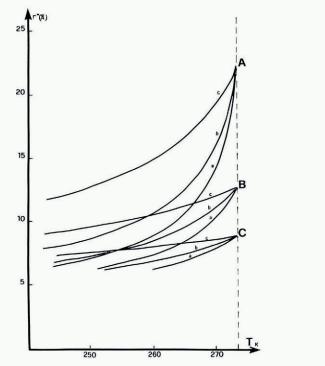

Fig. 1. Theoretical values of $r^\star$ versus temperature with $\gamma_1 = 4 \times 10^{-3} \, J \, m^{-2} \, (A)$, $7 \times 10^{-3} \, J \, m^{-2} \, (B)$, $10 \times 10^{-3} \, J \, m^{-2} \, (C)$ and $\Delta S_1 = 5 \times 10^5 \, J \, m^{-3} \, K^{-1} \, (a)$, $3 \times 10^5 \, J \, m^{-3} \, K^{-1} \, (b)$, $10^5 \, J \, m^{-3} \, K^{-1} \, (c)$.

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}r} = 0. \tag{3}$$

From Equations (2) and (3) the following result is obtained:

$$r^\star = \frac{-\gamma_1/2 + \left[(\gamma_1/2)^2 + \dfrac{\beta}{2\pi}\Delta S_1 \Delta T G b^2\right]^{\frac{1}{2}}}{\Delta S_1 \Delta T}. \tag{4}$$

This expression shows us that:

(i) $r^\star$ has the maximum value $\beta G b^2/2\pi\gamma_1$ at 273 K and, then, decreases with temperature;

(ii) the value of $r^\star$ is dependent on the physical parameters γ_1 and ΔS_1. These parameters are not known; nevertheless they have both an upper limit which is the surface energy of the interface ice–liquid water (i.e. c. 3×10^{-2} J m^{-2} at 273 K (Hobbs, 1974, p. 434), and the entropy of ice melting (i.e. 1.13×10^6 J m^{-3} K^{-1}) respectively.

The variation of $r^\star$ with temperature is shown in Figure 1 for several values of the parameters γ_1 and ΔS_1, always lower than the interfacial ice–water energy and the entropy of melting ice respectively; in these conditions the values of $r^\star$ are higher than those generally accepted in dislocation theory.

Furthermore, an example of the relation ΔG versus r is shown in Figure 2 where the four components of ΔG (Equation (2)) are distinguished.

It has been confirmed that all the values of $r^\star$ appearing in Figure 1 correspond to negative value of ΔG with E_c chosen to have $\Delta G = 0$ for $r = r_0$; this corresponds to a non-extended core energy between 0.1 and 0.3 eV per atomic length, which is an expected value.

Finally, it can be noted that for the small $r^\star$ obtained at low temperatures (for instance, curves c, Fig. 1) ΔG decreases and becomes of the order of kT per atomic length: hence, in such conditions, the extension of a dislocation core from r_0 to $r^\star$ is limited by thermal fluctuations; thus, the assumption of an extended core is only valid in a temperature range depending on values of γ_1 and of ΔS_1 and corresponding to curves of Figure 1.
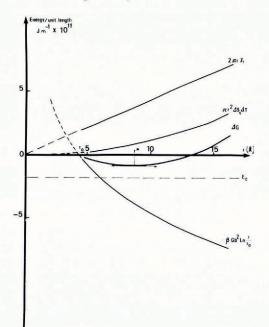

Fig. 2. *Variation of ΔG and of its components with r ($\gamma_1 = 7 \times 10^{-3}$ J m^{-2}, $\Delta S_1 = 3 \times 10^5$ J m^{-3} K^{-1} and $T = 260$ K).*

COOPERATIVE MOVEMENTS OF WATER MOLECULES IN THE CORE OF DISLOCATIONS

Due to the non-periodic arrangement of H_2O molecules in the dislocation cores, it was necessary to differentiate the ways by which these molecules can move.

Indeed, in a crystal, each atom or molecule may, owing to thermal activation, jump from a potential well towards a neighbouring one: each jump is independent from the others since the shape of potential wells is generally not affected by the jump (except for the neighbouring ones). The mean relaxation time is given by the relation (Fig. 3(a))

$$\tau_r = \tau_0 \exp(E_0/kT). \tag{5}$$

The approach is nevertheless different in the case of non-crystalline solids: the theory of disordered lattice (Zachariassen, 1932) indicates that the particles (atoms or molecules) are no longer in the positions corresponding to the minima of potential energy characteristic of the periodic arrangement, but are randomly distributed in the neighbourhood of such positions. Thus, each particle is in a metastable position related to the position of other particles (Fig. 3(b)) so that any of them, by moving, induces an increase in the mobility of the others within a certain distance (the correlation length).
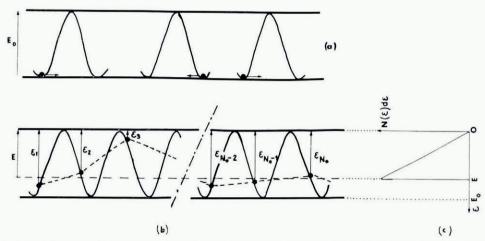

Fig. 3. Potential energy profile (a) in crystalline solid and (b) in a non-crystalline material with N_0 bonds; (c) linear distribution law of the values ϵ_i of bond energy.

Hence, a correlated movement of atoms or molecules (or a cooperative movement) corresponds to a change in the non-crystalline material from one configuration state to another.

Due to different concepts, several theories have emerged which lead to expressions for structure relaxation time other than the one given in Equation (5). The structure relaxation time being the mean time necessary for one particle to go from the initial to the final state of configuration, these various theories are as follows:

(a) The free-volume theory (Cohen and Turnbull, 1959): the non-crystalline solid contains free volume, the mean value of which is v_f, but this free volume is not regularly distributed. There are fluctuations, and when a critical free volume $v^\star$ is formed in a given number of atoms or molecules, a transition from one state of configuration to another is possible for the bulk, the relaxation time being given by

$$\tau(v_f) = \tau_{0f} \exp(v^\star/v_f). \tag{6a}$$

(b) The entropy theory (Adams and Gibbs, 1965): the system has a mean configurational entropy S, but, as in the above theory, fluctuations are considered. The cooperative movement of a number of atoms or molecules is possible when the entropy of configuration of the whole mass has the critical value $S^\star$; then the relaxation time of transition is given by:

$$\tau(S) = \tau_0 s \exp(S^\star/S).\tag{6b}$$

(c) The theory of excited bonds (Angell, 1971) was applied to non-crystalline solids with strongly directed bonds; the fraction of excited bonds c, is given by a thermodynamical equilibrium law. Once more, fluctuations may provoke the formation of domains in which all atoms or molecules can move cooperatively when the fraction of excited bonds is equal to a critical value $c^\star$. Then the structure relaxation time is

$$\tau(c) = \tau_{0c} \exp(c^\star/c).\tag{6c}$$

As hydrogen bonds in ice are directed, Equation (6c) is used to describe the cooperative movement of H_2O molecules in the non-crystalline extended core of dislocations. However the excited state of bonds must be specified. Eisenberg and Kauzmann (1969) considered structural models of water as a mixture; using such models, Angell (1971) took into account two types of bonds:

(i) a strong hydrogen bond corresponding to a disordered lattice of ice Ih (state 1);
(ii) a weak hydrogen bond corresponding to the excitation of the preceeding one so that a more dense packing of H_2O molecules (state 2) is obtained.

In the present case, it is assumed that the non-crystalline arrangement of H_2O molecules in the extended core of dislocations corresponds to the diagram in Figure 3(b). In fact, each H_2O molecule having two hydrogen bonds, it can be assumed that each molecule is represented by two neighbouring particles as in Figure 3(b). As a result, a distribution appears in the bonds energy ϵ. An example of a distribution not far from the true law is the simple linear distribution shown in Figure 3(c).

$$\mathcal{N}(\epsilon)\, d\epsilon = \frac{2N_0}{E^2}\, \epsilon\, d\epsilon,\tag{7}$$

where N_0 is the total number of bonds, ϵ the difference between the potential energy level of a given bond (state 1) and the level corresponding to the same bond when it is broken (state 2) whereas E is the difference between the most probable potential energy level and that corresponding to the broken bonds.

The thermodynamic equilibrium concentration in broken bonds (state 2) is given by:

$$c = \frac{1}{N_0} \int\limits_{0}^{E} \frac{\mathcal{N}(\epsilon)\, d\epsilon}{1+\exp(\epsilon/kT)} = \gamma(kT/E)^2,$$

where γ is a numerical factor equal to $\pi^2/6$ when $E \gg kT$ and about $\tfrac{3}{2}$ when E is between 0.10 and 0.15 eV.

The value of $c^\star$ then, has to be considered. To go from one state of configuration (I) to another (F), the only condition is that all the bonds concerned by the transition are broken in the state I; this leads to a value of $c^\star$ which is around one unit. Then, from Equation (6c) and with the above value of c, the structure relaxation time of a cooperative transition is found to be equal to:

$$\tau_r = \tau_0 \exp \frac{1}{\gamma} \left(\frac{E}{kT}\right)^2.\tag{8}$$

TRANSITION BY COOPERATIVE MOVEMENTS OF H_2O MOLECULES AND DISLOCATION GLIDE

It is possible, now, to consider a mechanism of glide of a dislocation having an extended core, by applying the above result to the case of a dislocation segment of length l. Figure 4(a) suggests a possible mechanism for glide in which the diameter of the extended core may change due to thermal fluctuations: in other words H_2O molecules may be constantly exchanging between the crystalline and the non-crystalline regions. Whenever no stress is applied, the mean position of a dislocation does not vary, but when stress is applied, there is a transformation into non-crystalline ice ahead of dislocation and "recrystallization" behind it. Concerning this mechanism the following assumptions are made:
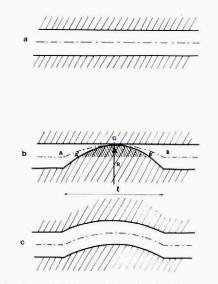

Fig. 4. *Movement of an extended dislocation:* (*a*) *initial position*, (*b*) *activated position, after which the dislocation is extended again* (*c*).

(i) Due to thermal fluctuation, n H_2O molecules of the core are rearranged in the crystalline state by cooperative movement so that an activated configuration, Figure 4(b) is obtained; then, the core is extended again as shown in Figure 4(c).

(ii) The average time necessary for such an activated configuration to be formed is

$$\tau_n \approx n\tau_1, \tag{9}$$

where τ_1 is the mean time necessary for the displacement of one molecule.

(iii) Occurrences of events corresponding to the two preceding assumptions may be found ahead and behind the dislocation line, but as previously indicated, the stress favours dislocation glide in the forward direction. The frequency of transition imposed by the stress in this way is, then (Eyring, 1936)

$$\nu = \frac{1}{\tau_n} f(\tau). \tag{10}$$

The factor $f(\tau)$ is usually taken in the form

$$f(\tau) = \exp\left(\frac{v_a\tau}{kT}\right) - \exp\left(-\frac{v_a\tau}{kT}\right) = 2\sinh\frac{v_a\tau}{kT}, \tag{11}$$

where $v_a\tau$ is the work done by the applied stress when the dislocation goes from (a) to (b) (Fig. 4), thus v_a is an activation volume.

With Equations (8), (9), (10), and (11), and taking τ_I equal to the value calculated in the preceding section (Equation (8)), the frequency of transition for dislocation segments of length l can be calculated,

$$\nu = \frac{2}{n\tau_0} \exp\left[-\frac{2}{3}\left(\frac{E}{kT}\right)^2 \right] \sinh \frac{v_a\tau}{kT}. \tag{12}$$

An estimate of τ_0 can be made either by considering it as the mean time for a molecule to be displaced with the sound velocity within one molecular distance ($\tau_0 \approx 7 \times 10^{-14}$ s) or by identifying it with the reverse of the most probable frequency of translational modes of vibration as indicated by spectroscopy (Fletcher, 1970, p. 137) ($\tau_0 \approx 2 \times 10^{-13}$ s).

An accurate value of n is more difficult to obtain. Actually, thermal fluctuations of variable strength are probable. The weakest fluctuations induce "recrystallization" of only one or a few molecules; the strongest, obviously less probable, may concern a larger number of molecules. If the weakest fluctuations only were to occur, the activation volume v_a would be small and lead to a linear dependence on the stress corresponding to the frequency of transition ν, i.e. the dislocation velocity. However non-linear dependence is experimentally observed, consequently consideration should be made also of the strong thermal fluctuations corresponding to the activated configuration introduced in assumption (i) and shown in Figure 4(b). In the case of this second type of fluctuations, the form of the activated configuration must be determined. Actually, it corresponds to the lowest free energy. Thus, when n is large, the "recrystallized" zone grows rapidly up to a width equal to $2r^\star$ and a length l. l must have an average value, taking into account both the effects of dislocation line energy and "recrystallization" energy. Indeed, the fluctuation energy would be too high both when l is small, due to the strong increase of dislocation line energy, and when l is large as a result of the large increase of "recrystallization" energy.

It is possible to estimate the energy of "recrystallization" from Equations (2) and (4), however the case is less clear for the dislocation line energy, which is a concept generally well defined only over a long distance. So it will be considered here that in the activated position (Fig. 4(b)) the form of the dislocation near the point C depends on the equilibrium between the line tension and the applied force since in this region the dislocaton core approaches the crystalline condition; hence, the radius of curvature is

$$R = \frac{Gb}{2\tau}.$$

A rough estimation of l can be made by applying this result to the whole loop. As $R \gg r^\star$ in the stress range generally used, the following value for l can be obtained:

$$l \approx 2(2r^\star R)^{\frac{1}{2}} = 2\left[\frac{Gbr^\star}{\tau}\right]^{\frac{1}{2}}. \tag{13}$$

In these conditions as shown in Figure 4, $v_a\tau$ can be taken to be of the order of $lr^\star\tau b/4$, which, by substitution of Equation (13) yields

$$v_a\tau = \tfrac{1}{2}(br^\star)^{\frac{3}{2}}(G\tau)^{\frac{1}{2}}, \tag{14}$$

Furthermore

$$n \approx \frac{\pi r^{\star 2} l/2}{b^3/3} = 3\pi \frac{r^{\star 2}}{b^3}\left[\frac{Gbr^\star}{\tau}\right]^{\frac{1}{2}}, \tag{15}$$

and the dislocation velocity v_d can be calculated from Equation (12)

$$v_d = \delta r^\star \frac{2}{n\tau_0} \exp\left[-\frac{2}{3}\left(\frac{E}{kT}\right)^2 \right] \sinh \frac{v_a\tau}{kT},$$

where δ is a numerical constant equal to $\frac{2}{3}$ if the dislocation is assumed to be a parabola in the activated position (Fig. 4(b)). Finally, with Equations (14) and (15) the following result is obtained:

$$v_d = \frac{4}{9\pi} \frac{1}{\tau_0} \frac{b^4}{(r^\star b)^{\frac{3}{2}}} \left[\frac{\tau}{G}\right]^{\frac{1}{2}} \exp\left[-\frac{2}{3}\left(\frac{E}{kT}\right)^2\right] \sinh \frac{(br^\star)^{\frac{3}{2}}(G\tau)^{\frac{1}{2}}}{2kT}. \tag{16}$$

DISCUSSION AND CONCLUSIONS

The preceding theoretical result (Equation (16)) is difficult to compare directly with experimental data since the physical factors E and $r^\star$ are not known, the latter depending on ΔS_1 and γ_1. However, the effect of shear stress appears to be correctly described by the present analysis.

Indeed, at low temperature (i.e. with low values of $r^\star$) and (or) at very low shear stress:

$$\sinh \frac{(br^\star)^{\frac{3}{2}}(G\tau)^{\frac{1}{2}}}{2kT},$$

is equivalent to

$$\frac{(br^\star)^{\frac{3}{2}}(G\tau)^{\frac{1}{2}}}{2kT}.$$

Then we have

$$v_d \approx \frac{2}{9\pi} \frac{1}{\tau_0} \frac{\tau b^4}{kT} \exp\left[-\frac{2}{3}\left(\frac{E}{kT}\right)^2\right], \tag{17}$$

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. This remark is in very good agreement with experimental data.

Equation (17) can be used to obtain E, from the temperature dependence of v_d observed by Maï (1976) at low stress and within a temperature range included between 251 and 270 K; the values $0.10 \text{ eV} < E < 0.11 \text{ eV}$ are obtained.

This result used in Equation (17) with $\tau_0 \approx 10^{-13}$ s, $\tau = 10^5$ N m^{-2} and $T = 255$ K yields the limits:

$$100 \text{ s}^{-1} < \frac{v_d}{b} < 1\ 700 \text{ s}^{-1},$$

which covers the range of experimental data as mentioned in the introduction. Actually Equation (17) is comparable to Equation (1) in which the relaxation time τ_r is replaced by

$$\tau_0 \exp\left[\frac{2}{3}\left(\frac{E}{kT}\right)^2\right].$$

The latter value is smaller than the former, which is in agreement with the qualitative predictions of Whitworth (1978).

It is interesting to note that the anelastic loss model (Weertman, 1963) leading to the relation (Whitworth, 1978):

$$\frac{v_d}{b} = \frac{4\pi^2}{G\tau_r\delta_{max}} \left[\frac{\zeta}{b}\right]^2 \tau,$$

where δ_{max} is the logarithmic decrement at the maximum loss and ζ is the width of the dislocation. This relation cannot correspond to the process limiting the movement since ζ being of the order of $2r^\star$, v_d/b would be about $9\ 000$ s^{-1} for the same experimental conditions.

Moreover, it is noticeable that Equation (17) is very similar to the one which would be obtained by assuming only a small fluctuation effect. In other words, in the present model, for small values of stress and (or) temperature large fluctuations are less probable, though more effective than smaller ones and anyhow, both lead to about the same velocity of dislocations.

In the range of non-linear behaviour, two other factors γ_I and ΔS_I should be defined from the stress dependence of v_d and from the variation of this stress dependence with temperature (Maï, 1976); both values have been determined, $\gamma_I = (6\pm1) \times 10^{-3}$ J m^{-2} and $\Delta S_I = (7\pm2) \times 10^5$ J m^{-3} K^{-1}.
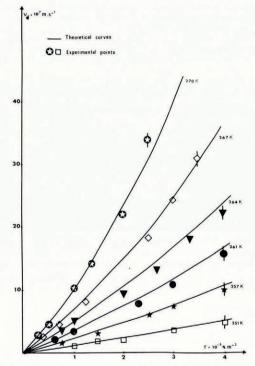

Fig. 5. *Dislocation velocity plotted against shear stress for various temperatures between 251 K and 270 K (experimental points and theoretical curves).*

These values of E, γ_I, and ΔS_I have been used in Equation (16) to draw theoretical curves $v_d = F(\tau, T)$; Figure 5 shows a comparison between the theoretical curves and Maï's experimental results (Maï, 1976).

It is noteworthy that ΔS_I and γ_I are, as predicted, lower than the entropy of melting of ice (1.1×10^6 J m^{-3} K^{-1}) and the ice–liquid-water interface energy ($c. 3 \times 10^{-2}$ J m^{-2}) respectively; moreover, E is nearer to the average bond energy of water ($c. 0.10$ eV) than to the bond energy of ice crystals (0.28 eV). In that case the linear distribution law (Equation (7)) is probably a too rough an approximation and no conclusion could be made concerning this point.

A theory on dislocation glide in ice must also take into account the effect of doping with substitutional impurities such as HF. It is well known that plastic behaviour of ice Ih is increased noticeably after addition of HF. Direct measurements of dislocation velocity in

HF-doped ice by X-ray topographic methods* have shown, on the one hand an increase of this velocity, and, on the other hand, an increase of its non-linear dependence on shear stress.

In the same work the effect of doping ice with HF has been analysed and the results can be summarized as follows:

(i) The concentration $[HF]_{nc}$ of HF in dislocation core is given as a function of the concentration $[HF]_c$ in the crystal by:

$$[HF]_{nc} = K_p[HF]_c,$$

K_p is the distribution coefficient; its calculation leads to a value of the order of 10^4. Thus, a strong effect of accumulation of HF molecules into dislocation cores is shown.

(ii) This accumulation induces a variation of the free energy given by:

$$\Delta G(HF) = -\pi r^2 (\Delta H_{HF} - T\Delta S_{HF}) K_p[HF]_c,$$

once more, only the upper limit of the parameter ΔH_{HF} is known: it is the enthalpy of dissolution of HF in water (3×10^9 J m^{-3} with infinite dilution); ΔS_{HF} is approximately the entropy of mixing of HF and H_2O molecules in dislocation cores.

(iii) Equation (2) must be modified in order to take account of $\Delta G(HF)$, then, another value of $r^\star$ is found in the case of doped ice:

$$r^\star(HF) = \frac{\gamma_1/2 + \left[(\gamma_1/2)^2 + \frac{\beta G b^2}{2\pi}(\Delta S_1 \Delta T - (\Delta H_{HF} - T\Delta S_{HF}) K_p[HF]_c)\right]^{\frac{1}{2}}}{\Delta S_1 \Delta T - (\Delta H_{HF} - T\Delta S_{HF}) K_p[HF]_c}. \quad (18)$$

It appears* that the presence of HF induces an increase of $r^\star$ which is, besides, less dependent on temperature.

Hence, the present analysis indicates that doping ice with HF involves an accentuation of the non-linear dependence on shear stress. These results are in agreement with experimental data obtained by Maï and others.*

Furthermore it is shown that doping ice with 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 assumption related to reorientation of the H_2O molecules (cf. Introduction) indicates, for the same doping, a factor of 10 to 100 depending on purity of non-doped ice.

It is useful to discuss the effect brought about by pressure P on the dislocation movement; as the transformation from the crystalline to the non-crystalline state corresponds to a decrease of volume ΔV_1 (per unit volume), the factor $\Delta S_1 \Delta T$ has to be replaced by $\Delta S_1 \Delta T - P\Delta V_1$ in Equations (2) and (4). This leads to a higher value of $r^\star$, i.e. a more stress-dependent velocity. Thus at moderate stress values, an increase of dislocation velocity in ice can be expected, and that may explain some experimental results concerning the effect of hydrostatic pressure on the plastic behaviour of ice single crystals (Hobbs, 1974, p. 282).

The preceding description of the movement of linear defects in ice is made with the simplifying hypothesis of the circular symmetry of the extended core of the dislocation; indeed, this hypothesis could be accepted in the case of pure screw dislocations, unless there is a large dissociation. In such a case, one can ask why these dislocations do not glide owing to the proposed mechanism in non-basal planes. In fact, such a movement is limited by the climbing mechanism, the dislocations being always, in practice, of mixed type. Nevertheless, this remark may explain some observations made by X-ray topography: $\frac{1}{3}a$ [11$\bar{2}$0] dislocations observed on a prismatic plane are neither parallel with one another, nor strictly perpendicular to c-axis.

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* Paper by C. Maï, J. Perez, J. Tatibouët, and R. Vassoille, entitled "Vitesse des dislocations dans la glace dopée avec HF", in preparation.

To sum up, a dislocation model with a non-crystalline extended core added to the assumption of cooperative movements of H_2O molecules seems, at present, to be the only model able to take into account all the experimental features of dynamic behaviour of dislocations in ice. Semi-quantitative results are obtained and can be applied to the study of microplasticity of ice (Vassoille and others, 1978). Moreover, this model may be useful in understanding some properties of ice, such as the dielectric properties of micro-crystals of ice (Lagourette, 1976) or ageing phenomena.

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DISCUSSION

R. W. WHITWORTH: I am much encouraged that attempts are being made to formulate a theory of the mobility of a dislocation with an amorphous core. However, I think that there is an important difference between your model and the type of process which I envisaged in my own paper. I suggest that molecules will be constantly exchanging between the amorphous and crystalline regions in a dynamic equilibrium. The stress must then in some way impose a bias on this process so that there is a net "melting" ahead of the dislocation and "recrystallization" behind it. As I understand your theory, you imagine a much larger region of amorphous material suddenly becoming crystalline behind the dislocation. This requires the coordinated movement of many molecules, and, as these molecules should be thought of as moving more or less independently in the amorphous region, this will be a rare event. I do not think that your equations take sufficient account of the fact that the probability of a fluctuation decreases with the number of molecules involved in it. In particular the mean time between such events will increase more rapidly than linearly with the number of independent components involved in the event. I believe that if due account were taken of the effects of the size of a fluctuation in the probability of its occurrence then frequent small changes are likely to have more effect than large rare ones.

J. PEREZ: Our model *also* corresponds to a dynamic equilibrium between H_2O molecules constantly exchanging between crystalline regions and non-crystalline core. The problem is to take into account the role of stress. We think that there are numerous small fluctuations but also some larger fluctuations. If we consider *only* the former (for instance when one H_2O molecule is concerned in the fluctuation), our model indicates a velocity given by

$$v_d \approx \alpha_1 \nu_D b \exp(-1/c) \sinh(\alpha_2 \tau b^3/kT) \approx \alpha_3 \nu_D(\tau b^4/kT) \exp(-1/c),$$

α_1, α_2, and α_3 being numerical factors about unity. This relation is comparable with that obtained in the previous models based on reorientation of H_2O molecules, but $1/\tau_D$ is replaced by $\nu_D \exp(-1/c)$, which may be higher, thus leading to values of velocity in agreement with experiment *save that the stress dependence is linear*. To interpret the non-linear behaviour, we must look to processes implying larger activation volume, that is to say larger fluctuations where a great number of molecules are concerned. Our assumption is that these molecules move in a correlated way (and not independently). So the average time required for the transition can be approached by the delay corresponding to the arrangement of one H_2O molecule multiplied by the number of molecules. In the present model, this number of molecules is calculated from the schematic activated position which corresponds to some sort of saddle point if we take into account the effect of line tension.

To sum up, this work is a first, very simplified approach supported by its applicability in interpreting, at least semi-quantitatively, our experimental data (dislocation velocity and internal friction) and still needing serious improvement.

S. J. JONES: In your theory, if NH_3 were dissolved in ice similarly to HF, would this not also increase $\nu^\star$ leading to an increase in dislocation velocity? This is unlikely to be the case because NH_3 is known to cause a hardening of ice single crystals (Jones and Glen, 1969).

PEREZ: We do not know the thermodynamic data for the dissolution of NH_3 in dislocation cores. Furthermore, this sort of dopant can form another phase or some sort of precipitates slowing dislocation glide. Nevertheless the best way to solve this problem is to measure, by X-ray topography, the velocity of dislocations in NH_3-doped ice and we hope to have the opportunity to do such an experiment.

J. PODZIMEK: I wonder about the value of γ_1 you assumed in the case of very small r. It was assumed that γ_1 is only a function of the temperature; however, in my opinion, it might be also a function of the size or curvature of the dislocation.

PEREZ: In our model it is difficult to know precisely what is the interface between the crystalline ice and the non-crystalline core. In those conditions we can do nothing but use an average value for γ_I, constant in our range of temperature and of $r^\star$ values. The application of the model to experimental data shows that this constant value of γ_I is very much lower than the ice–water interface energy.

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