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A QUANTUM MECHANICAL APPROACH TO THE VELOCITY OF
DISLOCATIONS IN ICE

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ABSTRACT

A quantum mechanical formulation is used to calculate the velocity of a kink on an otherwise straight dislocation line in ice. Treating the kink as a quasi-particle there exists the probability that it can tunnel through the potential barrier caused by unfavorable positions of the protons on the site just ahead of it. By unfavorable it is meant that the protons are arranged such that point defects occur if the kink proceeds. When an external stress is applied to the system there will be a net drift of the kink which advances the dislocation. The drift velocity thus calculated is in agreement with experimental evidence.

INTRODUCTION

Frost et. al ref. (1) and Whitworth et. al, ref. (2) have developed a theory for the velocity of dislocations in ice in the presence of an external stress by assuming an initially straight dislocation will advance due to the nucleation of pair of kinks. They derive the velocity of an isolated kink on the otherwise straight line dislocation and use the fact that this represents an upper limit for dislocation velocity, i.e., $v_{dis} \leq v_{kink}$. (For a discussion concerning this idea see Glen, ref. (3)). Their result for kinks is at least one order of magnitude smaller than the measured dislocation velocities, ref. (4,5). Frost et. al are forced to conclude that an essential physical process is missing from their model and that of Whitworth et. al.

We feel that a quantum mechanical approach is the correct way of handling the problem. The method developed by Gosar, ref. (6) in treating a kink as a quasi-particle in covalently bonded materials, e.g. germanium and silicon can be used for ice by replacing the covalent bond by a hydrogen bond. This is because each oxygen atom in ice is linked to four other oxygen atoms by hydrogen bonds. This quantum mechanical point of view leads to a kink velocity within the realm of experimental agreement.

The model we have of ice is a crystallographically ordered array of oxygen atoms, with a disordered arrangement of hydrogen atoms obeying the so called Bernal-Fowler rules, namely, (i) There are two hydrogen atoms near each oxygen atom, (ii) There is only one hydrogen atom on or near each line joining two neighboring oxygen atoms. Breaches of the Bernal-Fowler rules can be considered as producing defects in the structure of ice. A failure of the first rule corresponds to an ionic defect. An oxygen atom with three protons near it is a positive ion $(H_3O)^+$; one with only one proton is a negative ion $(OH)^-$. A failure of the second rule is called a Bjerrum defect or orientational defect. A bond with

two hydrogen is a D-defect; a bond with no hydrogen is an L-defect.

As shown in fig. (1), Bjerrum defects or ionic defects can be created when a dislocation and hence a kink moves through ice. This will happen when the proton on the neighboring site to which the dislocation moves is unfavorably bonded.

Treating the kink as a quasi-particle as in ref. (6) it has a probability for tunneling through the potential barrier of the unfavorable bond. In the absence of an applied stress the kink will be "trapped" between two unfavorable bonds in the following sense: If there are several favorable bonds between the two unfavorable bonds, the probability for a transition through a favorable bond will be much higher than that for an unfavorable bond. Thus, when the kink encounters an unfavorable bond it is more likely to reverse its direction rather than pass through it. (See fig. 2)). However, an applied stress, σ , will cause a net drift of the kink which will advance the dislocation.

QUANTUM MECHANICAL FORMULATION OF KINK VELOCITY IN ICE

We consider the motion of an isolated kink at site p on the straight line of a dislocation. Assume that the protons on the site to which the kink moves are unfavorably oriented. As in ref. (6) let $|p\rangle$ represent the system with a kink at site p . The state $|p+1\rangle$ is created from $|p\rangle$ by breaking one hydrogen bond and forming another. A rearrangement of the protons at the sites ahead of the kink is necessary so that the Bernal-Fowler rules are not violated. This will involve the tunneling of protons through the potential barrier of hydrogen bonds. The matrix element, w , for this process should be of the same order of magnitude as the matrix Γ for the tunneling process involved in the mobility of hydronium ions H_3O^+ in ice. For the motion of H_3O^+ is produced by the tunneling of one of its three protons through the potential barrier of

the hydrogen bond to its neighboring H_2O molecule. Gosar, ref. (7), finds that when lattice vibrations of the crystal are taken into account, $\Gamma = 6.2 \times 10^{-4}$ ev. In a later paper, ref. (8), it is found that $\Gamma = 5.4 \times 10^{-4}$ ev. So w must be of the order of 10^{-4} ev.

The model Hamiltonian for ice with one moveable kink on the straight line of the dislocation can be taken directly from ref. (6).

$$H = \sum_{\gamma} \omega_{\gamma} a_{\gamma}^{\dagger} a_{\gamma} - \sum_{\gamma, p} \omega_{\gamma} |p\rangle \langle p| [Z_{\gamma}^*(p) a_{\gamma} + Z_{\gamma}(p) a_{\gamma}^{\dagger}] \quad (\hbar=1) \quad (1)$$

$$- w \sum_p (|p+1\rangle \langle p| + |p-1\rangle \langle p|) - (\underline{\sigma} \cdot \underline{b}) \hbar a \sum_p |p\rangle \langle p|$$

where $a_{\gamma}^{\dagger}$ and a_{γ} are the creation and annihilation operators for phonons of frequency ω_{γ} in the mode γ , Z_{γ} are parameters that determine the deformation of the elastic medium, σ is the external stress, b is the Burger's vector, h is the height of the kink, and a is the distance between two neighboring sites. The third term in (1) describes the resonance between states $|p\rangle$ and $|p+1\rangle$ which leads to the kink tunneling. The last term in (1) represents the interaction of the kink with σ . The third term can be considered as a small perturbation to the kink motion; in which case the first order transition probability, $P_{p, p+1}$, that at time t the kink is at site $p+1$ due to tunneling from site p at $t = 0$ can be obtained, ref. (6). The transition rate $W_{p, p+1}$ for this process is given by

$$W_{p, p+1} = \lim_{t \rightarrow \infty} \frac{dP_{p, p+1}}{dt} \quad (2)$$

For temperatures higher than the Debye temperature $W_{p, p+1}$ may be approximated by

$$W_{p, p+1} = w^2 \left(\frac{\pi}{UkT} \right)^{1/2} \exp \left[-\frac{(\Delta E + U)^2}{4UkT} \right] \quad (3)$$

From Proctor, ref. (9), the Debye temperature of ice is 224K. The experimental measurements for the velocity of dislocations in ice ref. (3,4) with which we wish to compare our results were done at a temperature of $-18^{\circ} \text{C} = 255\text{K}$. Therefore (3) is valid for our purposes.

In (3) k is the Boltzman constant and T the temperature at which the kink moves. $\Delta E = -(\sigma \cdot b)ha$. U is approximately equal to (ref. (6))

$$U = \frac{\mu b^2 a}{2\pi} \left(\cos^2 \theta + \frac{\sin^2 \theta}{1-\nu} \right) \ln \frac{h}{2\rho} \quad (4)$$

where $\mu = 3.19 \times 10^{10} \text{ dyne cm}^{-2}$, $\rho = b/8$, θ is the angle between the Burger's vector b and the direction of the dislocation line, and ν the Poisson ratio. Taking $\theta = 0$, $a = b = 4.5\text{\AA}$, $h = \frac{(\sqrt{3})}{2}b$,

$$U = 0.36 \text{ ev.} \quad (5)$$

The drift velocity is then (ref. (6))

$$v_k = a (W_{p,p+1} - W_{p,p-1}) = \quad (6)$$

$$2aw^2 \left(\frac{\pi}{UKT} \right)^{1/2} \sinh \left[\frac{(\sigma \cdot b)ha}{2kT} \right] \exp \left[-\frac{[(\sigma \cdot b)ha]^2}{4UKT} \right] \exp \left[-\frac{U}{4kT} \right]$$

Various stresses were used in the experiments, ref. (4,5). It was found that for low stress the dislocation velocity varied linearly with the stress. When σ is small (6) reduces to

$$v_k = 2aw^2 \left(\frac{\pi}{UKT} \right)^{1/2} \frac{(\sigma \cdot b)ha}{2kT} \exp \left[-\frac{U}{4kT} \right] \quad (7)$$

From (7) we see that for small stress the kink velocity and hence the dislocation velocity is proportional to the stress. This is in agreement with the experimental measurements done in ref. (4,5). We also see that when the stress is zero there is no net drift ($v_k = 0$).

To calculate a value for v_k we take $T = 225 \text{ K}$, $w = 10^{-4} \text{ ev.}$, and $\sigma = .1 \text{ MN m}^{-2}$. Using (7),

$$v_k = 5.11 \times 10^{-6} \text{ m/sec} \quad (8)$$

The dislocation velocity will be less than or equal to (8). For a stress of $.1 \text{ MN m}^{-2}$ and temperature of 255 K Fukuda and Higashi ref. (4,5) observe a dislocation velocity of

$$v_{\text{dis}} (\text{exper.}) = 3 \times 10^{-7} \text{ m/sec} \quad (9)$$

It should be noted that the theory developed by Frost et al leads to for these values of σ and T

$$v_k = 2.1 \times 10^{-8} \text{ m/sec} \quad (10)$$

while that of Whitworth et al leads to

$$v_{\text{dis}} = 4.9 \times 10^{-9} \text{ m/sec} \quad (11)$$

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FIGURE CAPTIONS

Fig. 1 A portion of an ice lattice showing the point defects which would be created by the passage of a dislocation. The lattice obeying the Bernal-Fowler rules (1), but the passage of a dislocation (2) would create defects which can be seen in (3), a D-defect on BC^+ and an L-defect on CD^+ . An alternative end state for the passage of the dislocation (4), if the hydrogen atoms move along their bonds to prevent the creation of Bjerrum defects. Note the negative ionic state at C^- and positive ionic state at C. Open circles: oxygen atoms; dots: protons. (After Glen, ref. (3)).

Fig. 2 In the absence of an applied stress the kink is trapped between sites 2 and 4 since the probability for a transition from site 4 to 5 (and from site 2 to 1) is much less than that from site 4 to 3 (and from site 2 to 3).

Figure 1

A straight dislocation with a kink

- $\oplus$ Protons are favorably arranged
- $\ominus$ Protons are unfavorably arranged

h is the height of the kink and a is the distance between two sites

Figure 2

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