Observation of Dislocations in Ice

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The advantages and disadvantages of the three techniques used to examine dislocations in ice, *viz*., etch pitting–replication, transmission electron microscopy, and X-ray topography (XT), are reviewed, and it is shown that XT is the most useful of these techniques. The introduction of high-intensity synchrotron radiation for XT demonstrated that conventional XT observations are of dislocation structures which have undergone recovery. Some of the important dynamic observations and measurements of dislocations which have been made using synchrotron X-ray topography are outlined.

Introduction

An understanding of both the structure and dynamics of the dislocations in a material is fundamental to an understanding of its mechanical properties. Over the past 35 years, the structure and mechanical properties of both laboratory-grown and naturally-formed ice Ih have received considerable attention; see, for example, refs 1–3 for reviews. On a fundamental level, there have been several attempts to correlate the mechanical properties of ice with its internal defect structure.[4–11] Models have been produced which attempt to relate dislocation velocities in single crystals to the applied stresses[4–8] based on a knowledge of the possible dislocations and slip planes. One outcome of this modeling is that the measured dislocation velocities can be more accurately modeled if the dislocations are assumed to move on the glide set of planes (where they can, in principle, dissociate[12]) rather than on the shuffle set,[7] although, experimentally, it has not been determined on which set of the two types of basal planes the dislocations move.

While understanding single-crystal ice is important, naturally-occurring ice is polycrystalline, although the grain size can be very large (tens of millimeters). Only recently have studies attempting to correlate the internal defect structure with the mechanical properties of polycrystalline of ice been successfully initiated.[13–15] Of particular importance in polycrystals are both the mechanisms of grain boundary generation of dislocations and the interaction of gliding dislocations with grain boundaries. For example, the model used to explain the “brittle to ductile transition” in ice[10,11] is based on dislocation pile-ups, which have only recently been observed unambiguously.[15]

The purpose of this paper is to discuss the advantages and disadvantages of the techniques which have been used to examine dislocations in ice, and to present some of the more significant observations that have been made using the most useful technique for ice, that is, synchrotron X-ray topography.

Techniques for Dislocation Observation in Ice

Three techniques have been used to examine dislocation structures in ice: etch pitting–replication, transmission electron microscopy (TEM), and X-ray topography. The advantages and disadvantages of each technique are described below.

Etch Pitting. Etch pitting has been used for dislocation examination in a large number of materials. Etch pitting of ice involves coating the surface with a formvar solution. This produces a pit where a dislocation intersects the surface and forms a replica of the pit. Either the etch pit itself or the replica can then be examined using either an optical microscope or a scanning electron microscope. Etch pitting has revealed some valuable information about dislocations in ice, such as their density at zero or very low strains and the fact that dislocations play a role in the plastic flow of ice.

Etch pitting has been extensively used to examine nonbasal dislocations in ice.[16–19] However, the basal dislocations, which have the dominant role in viscoelastic flow, are difficult to observe. Etch tracks or grooves corresponding to moving dislocations can be observed, allowing estimates of dislocation velocities, but again these are produced by gliding nonbasal dislocations.[19]

In addition to the difficulty of “imaging” basal dislocations, the etch-pitting technique has three major problems. First, three-dimensional dislocation arrangements are characterized solely by surface examination. Thus, a dislocation expanding under a shear stress may produce only a single etch pit regardless of the length of the dislocation; etch pitting used to reveal this dynamic behavior would probably cause the dislocation to be pinned at the surface. Also, a dislocation loop which does not intersect a surface would not be observable at all. In addition, Sinha[19] has pointed out that poor surface preparation can produce changes in the surface defect structure. Second, the size of the etch pits, typically $>3\ \mu$m, places an upper limit on the dislocation density that can be examined of $\sim 10^{11}$ m^{-2}. Third, interpretation is often difficult. For example, features around a deformed notch where no etch pits are present have been interpreted as being either dislocation free zones or having a very high dislocation density.[20,21] Also, etch pitting–replciation studies purportedly showing dislocation pile-ups against GBs[21] may have actually revealed GB emission of dislocations. Sinha[17,19] refined the etch-pitting technique so that “whiskers” of formvar corresponding to the dislocation core can be produced at the bottom and the sides of etch pits. This whisker technique can reveal both basal and nonbasal dislocations and indicate the three-dimensional structure of the dislocations. It also allows higher dislocation densities to be examined: for 0.25 μm whiskers, up to, say, 10^{13} m^{-2}. However, the refined technique is still limited to revealing dislocations which intersect a surface and complex dislocation arrangements are difficult to view.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) is a practical application of Braggs’ law for imaging crystals and utilizes a single energy or wavelength of electrons incident on the specimen. The resulting micrographs are two-dimensional projections of the three-dimensional struc-

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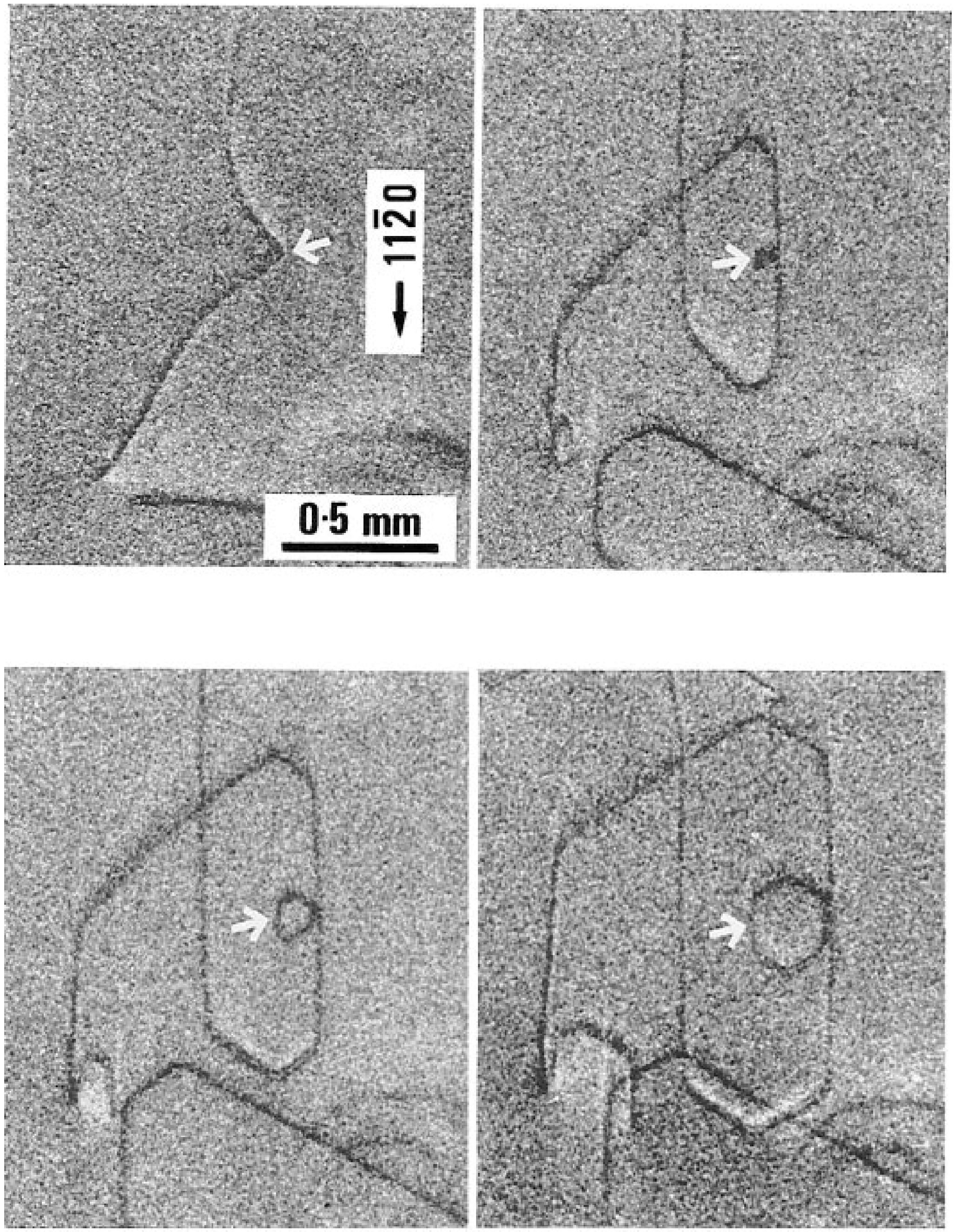

Figure 1. A Frank–Read source. Plane of projection (0001). The Burgers vector, the diffraction vector, and the shear stress are in the [11$\bar{2}$0] direction shown. The point marked by the white arrows remains fixed as the two dislocation segments spiral around it. From ref 35.

ture of a material. The attraction of this technique is its high resolution. For example, using the weak-beam technique dislocation image widths of ∼1 nm can be obtained and, thus, if dislocations dissociate into partials, the partials can be resolved if their separation is greater than ∼1.5 nm. In ice, there are two types of basal planes on which slip could occur, the so-called shuffle planes and the glide planes. The planes of the shuffle set are more widely spaced, but the packing in the glide set resembles that in a close-packed hexagonal metal. Dislocations in the glide set can potentially lower their self-energy by dissociating into two partials of $(a/3)\langle 01\bar{1}0\rangle$ type. For example, the $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ screw could dissociate into two 30° partials, whereas the $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ 60° dislocation would dissociate into an edge partial and a 30° partial. Fukuda et al.[22] have estimated that the separation of these partials is around 20 nm. Thus, the particular appeal of TEM for ice is that the dissociation of a $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ dislocation into $(a/3)\langle 0\bar{1}10\rangle$ partials would be clearly observable.

There are three intrinsic problems associated with the use of a TEM to study ice. First, it is difficult to transfer ice specimens to the TEM and keep them there without either sublimation or frost formation. Second, ice is sensitive to damage by the electron beam.[23] Third, it is very difficult to prepare thin foils from bulk samples. Finally, since electrons interact strongly with matter, the maximum usable thickness of a specimen is ∼1 μm. Thus, there is some question whether TEM specimens this thin can be representative of bulk ice.

TEM studies of ice have revealed[23,24] dislocations, stacking faults, cavities due to the electron irradiation, and brine pockets (in ice grown from salt water). However, these features have been observed in samples produced either by condensing water vapor onto a cold substrate in the TEM or by making a thin film from water rapidly frozen between polymer film-covered grids. There have been no published attempts of examinations of dislocation structures from deformed material.

X-ray Topographic Studies of Ice. Similar to the TEM, X-ray topography (XT) is a practical application of Braggs' law, and X-ray topographs are two-dimensional projections of the three-dimensional structure of a material. Ice is a particularly suitable material for X-ray topographic study for three main reasons. First, it has a relatively low molecular weight and, hence, a low X-ray absorption coefficient, allowing the use of thick specimens and, hence, allowing bulk deformation to be observed. Second, crystals can be grown with a sufficiently low dislocation density so that the motion of individual dislocations can be followed. Third, since in ice the dislocation velocity is proportional to the applied stress (at least over the stress range which has been studied), dislocations in ice can be made to move slowly enough to be observed under stress.

Conventional XT, which typically involves scanning the ice crystal with a weak monochromatic X-ray beam, was first applied to the observation of dislocations in ice by Hayes and Webb[25] and has made useful contributions ever since. Grown-in dislocations in both naturally-formed and laboratory-grown ice have been shown to have mostly $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ Burgers' vectors and are usually in stable networks. In addition, circular loops or spiral dislocations with [0001] Burgers' vectors are sometimes observed.[26] The circular loops, which lie on the basal plane, are of prismatic character and are formed by interstitial condensation during cooling. Faulted dislocation loops with a Burgers' vector and corresponding fault vector of $^1/_2$[0001] have also been observed. The observation of wide stacking faults by XT in single crystals of ice led to the study of point defects and provided a method for determining the energy of stacking faults. Observations of the expansion and contraction of faulted and unfaulted dislocation loops due to point defect diffusion have yielded the best values of the parameter for the self-diffusion of interstitials in ice (detailed in the reviews in refs 26 and 27).

The deformation mechanisms in single-crystal ice have been fairly well established using conventional XT.[26] Slip dislocations in ice have been shown to have a $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ Burgers' vector. Dislocations can slip either on the basal plane or on nonbasal planes, such as the prismatic planes. The edge segment on the nonbasal plane was also shown to move faster than the screw dislocation on the basal plane. This plays an important role in deformation since it provides the principal mechanism for the generation and multiplication of the dislocations which subsequently move on the basal planes and produce macroscopic basal slip. In addition, features such as dislocation generation at inclusions have been documented.[26]

Most early progress related to the deformation of ice containing a large-angle grain boundary was made by Higashi's group[26,27] at Hokkaido University in Japan. Upon stressing bicrystals, strain fields, facet structures, and both dislocation generation and absorption were observed at high-angle grain boundaries. The strained (darkened) areas at the grain boundaries were also observed to extend into the grain interior upon further loading.

The problem with conventional XT is that exposure times are long, typically greater than 10 min. This means that for observations above −30 °C substantial recovery takes place. This method is unable to reveal the true dislocation behavior in ice under stress, as indicated by the topographs which show blurred images and/or curved dislocations and the formation of small-angle grain boundaries after deformation and load removal. The images from conventional XT are not easily interpretable due to these recovery effects. Straight dislocations which lie in Peierls valleys, see below, are rarely seen after deformation.

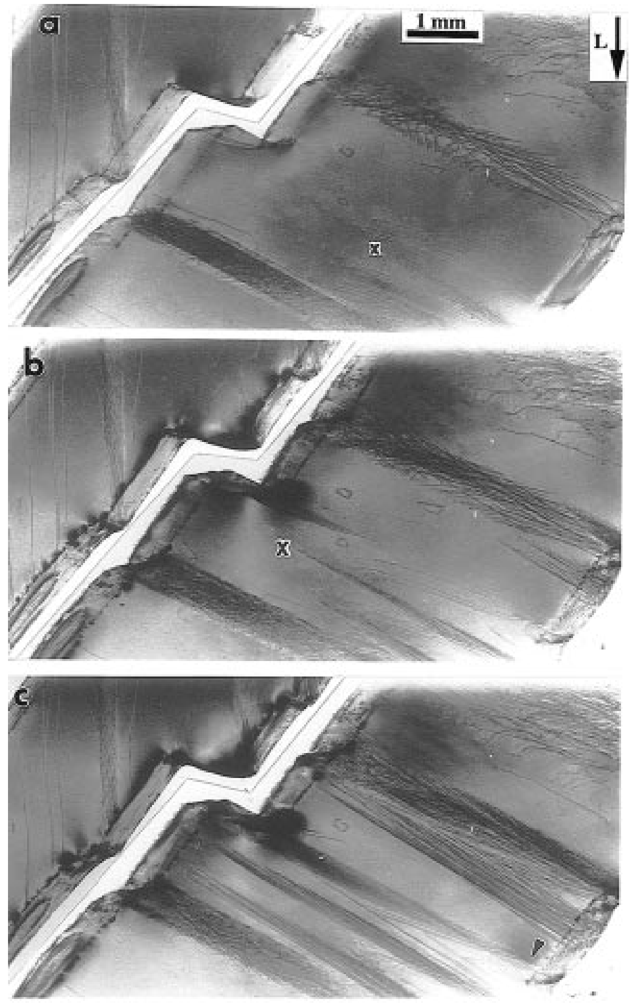

Figure 2. X-ray topographs taken at −6.0 °C at increasing load (marked L) showing basal dislocations which have been emitted at grain boundary facets into two adjacent grains in order to accommodate grain boundary sliding. Note, in particular, the dislocations in the slip bands labeled X which have nucleated at the grain boundary facet arrowed in the lower right and which have traversed across the lower grain progressively further in a, b, and c. After ref 13.

Synchrotron X-ray Topography. Synchrotron XT, performed using either monochromatic radiation or white radiation, is a much simpler technique than conventional X-ray topography. There are two key features of this technique. First, the high intensity of synchrotron-produced X-rays allows exposure times of ~2 s, enabling dynamic experiments and unrecovered dislocation structures to be observed. Second, synchrotron-produced X-rays are highly collimated, with a beam divergence angle of only several tens of arc second in a direction orthogonal to the plane of the synchrotron storage ring. This is several orders of magnitude smaller than the divergence angle from a conventional X-ray source and results in images with both higher spatial resolution and higher angular resolution than images from a conventional source.

Synchrotron XT was first applied to ice by Whitworth and co-workers[28] using the white-beam Laue transmission geometry in which each diffraction spot contains an image of the specimen. The setup for monochromatic radiation is similar to that for white radiation except that the specimen has to be precisely positioned so that a particular set of planes satisfy Braggs' law for the wavelength used. A key physical limitation with the monochromatic technique is that, typically, only one crystal can be imaged and only one diffraction spot can be produced from that crystal at a time. Thus, the monochromatic method is more limited in its application than the white-beam

Figure 3. X-ray topograph showing the generation of both semihexagonal basal dislocation loops and nonbasal edge segments at grain boundaries. The grain boundaries are almost black due to the large local stress concentrations. Interestingly, semihexagonal basal dislocation loops have also been nucleated at the grain boundaries even though the resolved shear stress from the far-field applied stress is close to zero. Temperature was −6.1 °C. After ref 13.

technique. However, defect contrast is somewhat easier to interpret when using monochromatic X-rays.

Higashi's group[29,30] used the synchrotron XT to extend their previous conventional XT studies of prismatic dislocation loops formed in ice single crystals by the condensation of point defects at temperatures from −1 to −5 °C. Whitworth's group[28,31−35] used synchrotron XT to observe the dynamic behavior of dislocations. Topographs of the operation of Frank−Read sources, Figure 1, and of the glide of the fast edge dislocations on nonbasal planes clearly showed the mechanisms of dislocation generation and multiplication in high-quality ice single crystals. It was also shown that under stress screw and 60° basal dislocations with $\langle 11\bar{2}0\rangle$ Burgers' vector predominate in ice, rather than the curved dislocations typically observed by conventional XT. The observation that basal screw dislocations do not cross-slip and glide on nonbasal planes is strong evidence that they are widely dissociated on the basal plane, and, hence that slip occurs on planes of the glide set.

Dynamical straining experiments[32] of stressed single crystals of ice have been used to disclose values of dislocation velocities as a function of both stress and temperature. Interestingly, only a single measurement, thus far, has indicated that dopants, such as HCl, can affect dislocation velocity in ice.[36] Most measurements suggest otherwise,[32,35] even though small quantities of dopants strongly affect the mechanical properties.[37−39]

Only recently has synchrotron XT been used to study polycrystalline ice.[13−15] When performing synchrotron white beam XT on a polycrystal, each grain produces a Laue pattern. *In situ* straining of polycrystalline ice has shown that grain boundary regions always deform before the grain interiors; see Figures 2 and 3. This process overwhelms the dislocation multiplication mechanism in single-crystal ice, suggesting that previous studies of deformation of single-crystal ice may have limited relevance to the deformation of polycrystals.

For polycrystals, three different situations are possible. First, for grains and grain boundaries which are not oriented in any special relationships with the loading direction, screw and 60° basal $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ dislocations are emitted from grain boundary facets (Figure 2). These dislocations are emitted in order to accommodate grain boundary sliding which leads to stress concentrations at the grain boundary facets. Eventually, the dislocations which have been emitted traverse the grain and pile-up at the opposite grain boundary. The pile-ups have been shown to relax upon annealing.[79]

The second situation is when basal slip is suppressed when the resolved shear stress on basal slip systems is close to zero. This occurs when the loading direction is nearly perpendicular to either the basal plane or to the basal plane normal. In this situation, nonbasal $(a/3)\langle 2\bar{1}\bar{1}0\rangle$ dislocations can be emitted from grain boundary facets. Figure 3 shows the glide of the nonbasal dislocations occurs by the fast movement of short edge segments which trail screw segments behind them.

The third situation occurs when grain boundary sliding is suppressed. In that case, there are no stress buildups at and consequent dislocation emissions from grain boundary facets. Then, under the correct, and somewhat exacting, geometrical conditions, i.e., some alignment of the basal slip planes in the two grains, slip transmission can occur.

Conclusions

Synchrotron XT appears to be ideal for the study of defects in ice. It suffers from only one disadvantage; that is, X-ray extinction distances are large. Thus, the images of dislocations in ice are typically 20 μm in width. This means that the technique is usually confined to high-quality crystals which have been carefully grown and handled to ensure a very low dislocation density ($<10^9$ m^{-2}). The wide images also mean that dislocations cannot be resolved into partials and that dislocation loops less than 20 μm in diameter cannot be resolved. Even with these limitations, there are numerous potential areas of study of ice by synchrotron XT.

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