The effects of sulfuric acid on the mechanical properties of ice single crystals

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ABSTRACT. Ice single crystals of various orientations containing various concentrations of H_2SO_4 up to 11.5 ppm were cut from large pucks of laboratory-grown ice. Constant-strain-rate compression tests were performed on the doped ice crystals both at $-20°C$ at an axial strain rate of $1 \times 10^{-5} \, s^{-1}$ and at $-10°C$ at $1 \times 10^{-6} \, s^{-1}$. The stress–strain curves showed a linearly rising stress with increasing strain, followed by a sharply declining stress after reaching a peak. With further strain, the sharp decline in stress slowed. The tests clearly showed, for the first time, that this naturally occurring impurity dramatically decreases both the peak stress and the subsequent flow stress of ice single crystals. The decrease in the peak strength was related to the square root of the concentration of H_2SO_4 up to 11.5 ppm, suggesting that the solubility limit of H_2SO_4 in ice is at least 11.5 ppm. The sulfuric acid also appeared to increase the ductility of the ice. Preliminary examination of a doped ice single crystal by synchrotron X-ray topography suggested that sulfuric acid dramatically increases the grown-in dislocation density.

INTRODUCTION

To understand how impurities affect the mechanical behavior of ice is important since a number of impurities exist in natural ice. Dissolved impurities in ice can occur either as substitutional ions in the lattice, like F^- and NH_4^+, or as interstitials, like SO_4^{2-} and NO_3^-. Impurities in the lattice can, in principle, either act as obstacles to the movement of dislocations or aid in dislocation motion, and therefore influence their mechanical properties.

Glen (1968) pointed out that proton disorder in crystals of ice Ih presents the major obstacle to dislocation glide. Adjacent (0001) glide planes are connected through randomly oriented hydrogen bonds. Therefore, in order for a dislocation to move, the hydrogen bonds have to be appropriately reoriented. This bond reorientation occurs by the movement of ions (H_3O^+ and OH^-) and Bjerrum defects (D type and L type). Petrenko and Schulson (1992) used an electrical technique to study the effect of point defects on dislocation mobility and found that ice becomes harder when point defects are extracted, suggesting that dislocation mobility was directly related to protonic rearrangement.

Following Glen's model, it is evident that impurities that introduce additional point defects into ice should increase the mobility of dislocations. For example, each HF molecule introduces one L-defect, and the H_3O^+ concentration also increases (Gränicher 1963). Thus, Jones (1967) and Jones and Glen (1969) demonstrated that very small amounts of dissolved impurities (HF and NH_3) could strongly affect the mechanical properties of ice single crystals. For example, at $-70°C$ and a constant strain rate of $2.7 \times 10^{-7} \, s^{-1}$, 50 ppb of HF decreased the peak stress by one-third, and with 8 ppm of HF the peak stress was only about one-quarter that of pure ice. The HF reduced the subsequent steady-flow stress even more. Jones and Glen (1969) argued that the additional point defects introduced by the HF increased the probability of bond reorientation, allowing the bonds to assume the correct orientation for

a dislocation to pass. Therefore, the dislocations moved faster and the HF-doped ice crystals became softer.

Jones and Glen (1969) demonstrated that the effect of HF was not due to the grown-in defects from the melt, through the following experiment. They strained pure ice and then unloaded it. They then doped the specimen with HF, and, upon retesting, a dramatically smaller stress was required to maintain the same strain rate. On the other hand, if the specimen was simply annealed without doping with HF, further plastic deformation continued at a stress close to that prior to the interruption. However, Jones and Glen did not show whether the introduction of HF increased the dislocation density. Later, using conventional X-ray topography, Maï and others (1978) found that the velocity of dislocations in ice doped with 10 ppm HF was double that in pure ice. However, as pointed out by Ahmad and Whitworth (1988), the results of Maï and others are ambiguous due to the long image-acquisition time during which dislocation recovery may have occurred. Therefore, it is still not clear whether the increase in dislocation density or the increase in dislocation mobility causes the softening effect from HF.

Nakamura and Jones (1970, 1973) also demonstrated a softening effect in the temperature range $-5°$ to $-26°C$ by doping ice single crystals with 5–12 ppm HCl. Both Jones and Gilra (1972, 1973a, b) and Oguro (1988), using conventional X-ray topography, found that the addition of dopants (HF, HCl, NH_3) greatly increased the grown-in dislocation density in ice. Using synchrotron X-ray topography, Shearwood and Whitworth (1992) found that 0.036 ppm HCl had no effect on the dislocation velocity in ice single crystals between $-30°$ and $-55°C$. But for this amount of dopant they found that the dielectric relaxation time was reduced by about an order of magnitude, with a lower activation energy. Later, Hu and others (1995), also using synchrotron X-ray topography, confirmed that low concentrations of HCl (0.020 ppm) had little effect on dislocation velocity in ice. In

contrast, a single measurement at $-16°C$ on ice doped with 7 ppm HCl showed an increase in the dislocation velocity by almost an order of magnitude compared to pure ice. However, the large dislocation density present in the latter case could have affected the motion of individual dislocations.

Although work on HCl and HF is of interest in elucidating the mechanisms of dislocation motion in ice, these impurities do not generally occur in natural ice. In contrast, sulfuric acid is present in natural ice, arising from aerosols produced by volcanoes. It is known that sulfuric acid is present in ice at the triple junctions where three grains meet (Mulvaney and others, 1988; Wolff and others, 1988; Fukazawa and others, 1998). A substantial concentration of sulfuric acid (>1 M in areas of 1 μm^2) was found, using energy-dispersive spectroscopy in a scanning electron microscope as a solid phase at the triple junctions of ice from Dolleman Island held at $-160°C$ (Mulvaney and others, 1988). The presence of the sulfuric acid at the triple junctions could explain the electrical properties of Antarctic ice.

By introducing point defects into ice, sulfuric acid might also be expected to influence both dislocation nucleation and mobility and, concomitantly, affect the mechanical properties of ice crystals. The effects of H_2SO_4 on mechanical behavior, dislocation nucleation and dislocation mobility have not been reported for either polycrystalline or single crystal ice. The purpose of the research presented here is to show how sulfuric acid affects the mechanical properties of ice single crystals.

EXPERIMENTAL

Distilled water was mixed with sulfuric acid, and its acidity was measured using a pH meter. Large pucks (28 cm diameter, 13 cm high) of various concentrations of H_2SO_4-doped ice were grown using the same method as that used to grow undoped ice, as described elsewhere (Trickett and others, in press). Ice single crystals with various orientations were cut from the pucks. The concentrations of sulfuric acid in the ice single crystals were determined using the pH meter on the crystals which were melted after mechanical testing. Using polarized light, all the single crystals appeared to be of high quality.

Compression specimens, 60 mm high by 25 mm wide by 20 mm deep, were prepared from the single crystals as described elsewhere (Trickett and others, in press). The crystal specimens were prepared with the basal plane tilted at an angle from the top face of the crystal by $\theta = 3°, 25°, 33°$ or $80° \pm 1°$ (see Trickett and others, in press) and with dopant levels of 0.1, 4.4, 6.8 or 11.5 ppm of H_2SO_4. Compression tests were performed at a constant axial strain rate of either $1 \times 10^{-5} s^{-1}$ at $-20°C \pm 0.5°C$ or $1 \times 10^{-6} s^{-1}$ at $-10°C \pm 0.5°C$ on a Materials Testing System located in a cold room. For purposes of comparison, similar undoped specimens were also produced and tested.

The dislocation structures in some of the doped ice single crystals were examined using white-radiation synchrotron X-ray topography at the National Synchrotron Light Source at Brookhaven National Laboratory for Nuclear Research, Long Island, NY, U.S.A. The specimen preparation and operating conditions for the X-ray topography have been described in detail elsewhere (Liu and Baker, 1993; Liu and others, 1993).

RESULTS AND DISCUSSION

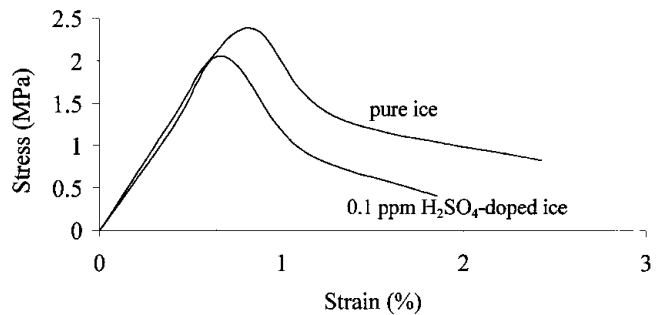Figure 1 shows typical engineering stress–strain curves

Fig. 1. Engineering stress–strain curves for undoped and H_2SO_4-doped (0.1 ppm) ice single crystals with $\theta = 80°$ at $-10°C$ and an axial strain rate of $1 \times 10^{-6} s^{-1}$.

obtained at $-10°C$ at a constant strain rate of $1 \times 10^{-6} s^{-1}$ for two identically oriented ($\theta = 80°$) ice single crystals, one containing 0.1 ppm H_2SO_4 and the other undoped. Both curves showed typical behavior for ice deforming by basal slip, i.e. a linearly rising stress with increasing strain, followed by a sharply declining stress after reaching a peak. With further strain, the sharp decline in stress slowed. Comparison of the two curves shows that even 0.1 ppm of H_2SO_4 decreases both the peak stress and the subsequent flow stress at $-10°C$. Interestingly, the two curves appear to be diverging with increasing strain.

Crystals with various concentrations of H_2SO_4 were strained in order to examine the relationship between the dopant level and the strength. Figure 2 shows the situation for $\theta = 3°$ where it is clear that the higher the dopant level, the softer is the doped ice. Also, note that both of the pure ice crystals fractured at or near the peak stress (fracture is indicated by a vertical arrow), whereas only two of the doped-ice crystals fractured during testing (at greater plastic strains than for undoped ice). Figure 3 shows data for crystals with $\theta = 33°$ both undoped and doped with 4.4 ppm H_2SO_4. For this orientation and dopant level the peak stresses are only slightly reduced by the dopant, although the subsequent flow stress is clearly reduced. It is evident that the acid has a less significant softening effect at $\theta = 33°$ than at $\theta = 3°$, i.e. H_2SO_4 doping has a more
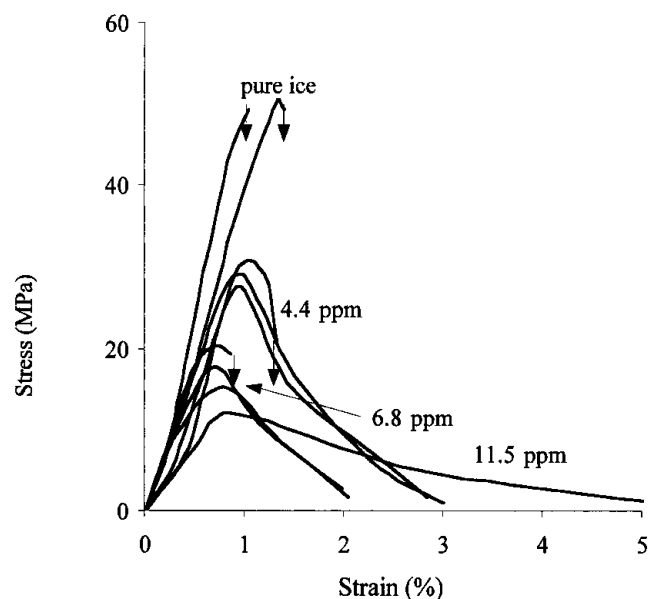

Fig. 2. Comparison between the engineering stress–strain curves for pure and H_2SO_4-doped ice single crystals of various concentration with $\theta = 3°$ at an axial strain rate of $1 \times 10^{-5} s^{-1}$ at $-20°C$.
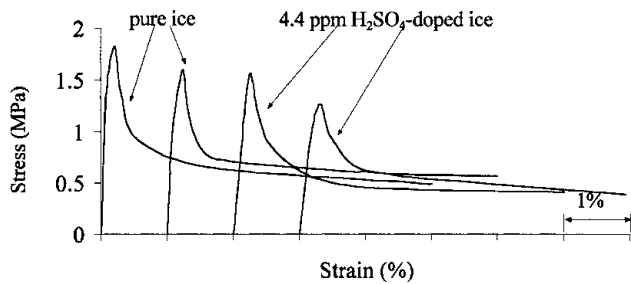
Fig. 3. Comparison between the engineering stress–strain curves for pure and H_2SO_4-doped (4.4 ppm) ice single crystals with $\theta = 33°$ at an axial strain rate of $1 \times 10^{-5} \, s^{-1}$ at $-20°C$. The curves are offset along the strain axis for clarity.

pronounced influence on the flow of ice crystals with a hard rather than a soft orientation.

The difference between the peak critical resolved shear stress (CRSS) for undoped ice and that for H_2SO_4-doped ice, i.e. $\Delta\sigma = \sigma_p^{\text{pure}} - \sigma_p^{\text{dopant}}$, at $\theta = 3°$, normalized to a shear strain rate of $1 \times 10^{-5} \, s^{-1}$ (see later), is plotted as a function of the square root of the concentration of H_2SO_4 in Figure 4. $\Delta\sigma$ increases linearly with the square root of the concentration of H_2SO_4 in ice up to 11.5 ppm. This suggests that even at 11.5 ppm, the H_2SO_4 is still in solution. Parabolic defect hardening in metals can often be described by $\Delta\sigma = \beta\mu c^{1/2}$, where μ is the shear modulus, c is the concentration of solute and β defines the strength of the hardening (Fleischer, 1963). Typically $\beta = 0.2$ for interstitial hardening and 0.002 for substantial strengthening. Using a value of $\mu = 7$ GPa for ice, Figure 4 yields a value of $\beta = 0.014$. This is less than that for interstitial strengthening, but much greater than that for substitutional strengthening in metals ($\beta = 0.001$). Although metals exhibit parabolic hardening from solutes, and ice shows parabolic softening, the mechanisms are quite different. Parabolic hardening in metals arises from the dislocation line being held up at solute atoms and having to bow out in the slip plane before the dislocation can break away. The solute softening in ice presumably arises from the additional L-defects and H_3O^+ ions allowing more rapid hydrogen-bond reorientation, thus easing dislocation passage along a slip plane. The $c^{1/2}$ dependence of the solute softening in ice presumably arises because the softening is inversely related to the separation of solute ions on the slip plane, which itself is inversely proportional to the square root of the solute atom concentration.
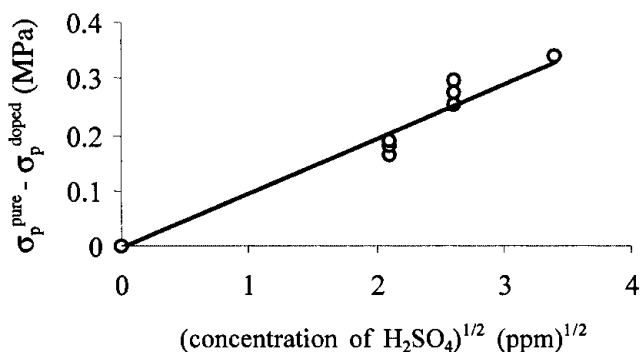

Fig. 4. Graph of the difference in CRSS (peak stress) between undoped ice and H_2SO_4-doped ice crystals ($\sigma_p^{\text{pure}} - \sigma_p^{\text{doped}}$) at $\theta = 3°$ vs the square root of the concentration of H_2SO_4 for crystals compressed at $-20°C$ normalized to a shear strain rate of $1 \times 10^{-5} \, s^{-1}$.

In an earlier paper (Trickett and others, in press), it was shown that the orientation dependence of the CRSS (peak stress) of high-purity ice single crystals obeyed Schmid's law. Thus, H_2SO_4-doped ice single crystals with various orientations were tested to see whether Schmid's law applies to doped ice. Figures 5 and 6 show typical resolved shear-stress–shear-strain curves for two different dopant levels at different orientations, while Figure 7 is an example of engineering stress–strain curves at the same orientation for 6.8 ppm H_2SO_4-doped ice and undoped ice. In order to make comparisons between the CRSS at different orientations, it is necessary to normalize the peak stresses measured at a constant compressive axial strain rate to a fixed shear strain rate (Trickett and others, in press). This was done by using a relationship between the shear stain rate, $\dot{\gamma}$, and the CRSS, τ, of $\dot{\gamma} \propto \tau^{1.9}$ (Trickett, 1999). The resolved shear stress–strain curves were thus normalized to a shear strain rate on the basal slip plane of $1 \times 10^{-5} \, s^{-1}$.

The peak CRSS normalized to a shear strain rate of $1 \times 10^{-5} \, s^{-1}$ is plotted as a function of angle θ in Figure 8. The peak CRSS of H_2SO_4-doped ice crystals, unlike that of undoped ice single crystals (Trickett and others, in press), depends on their crystallographic orientation, i.e. Schmid's law is not obeyed (if it was, the CRSS would be independent of θ for a particular dopant level). It is also clear from Figure 8 that, as noted earlier, H_2SO_4 has a more significant softening effect at $\theta = 3°$ than at $\theta = 25°$ or 33°. This suggests that the dislocation nucleation and multiplication mechanisms are different in a hard orientation (when the applied stresses are very high) than in a soft orientation (when the applied stresses are very low). Exactly how the mechanisms differ is unclear.
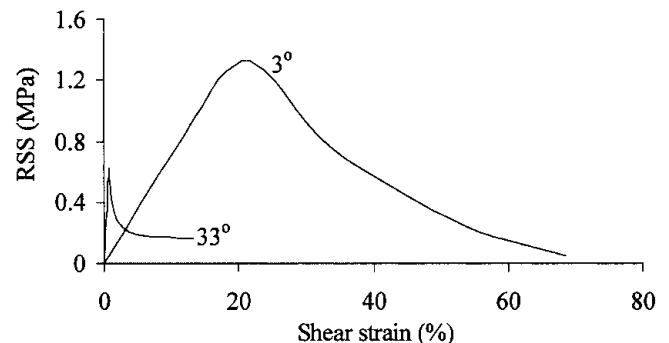

Fig. 5. Comparison between the resolved shear stress–strain curves for H_2SO_4-doped (4.4 ppm) ice single crystals with $\theta = 3°$ normalized to a shear strain rate of $1 \times 10^{-5} \, s^{-1}$ at $-20°C$.
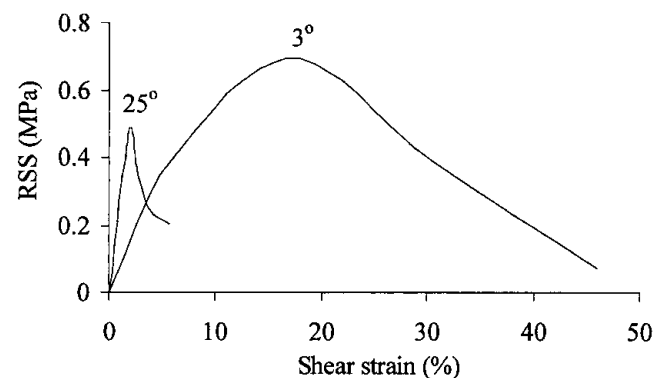

Fig. 6. Comparison between the resolved shear stress–strain curves for H_2SO_4-doped (6.8 ppm) ice single crystals with $\theta = 3°$ and $25°$ normalized to a shear strain rate of $1 \times 10^{-5} \, s^{-1}$ at $-20°C$.
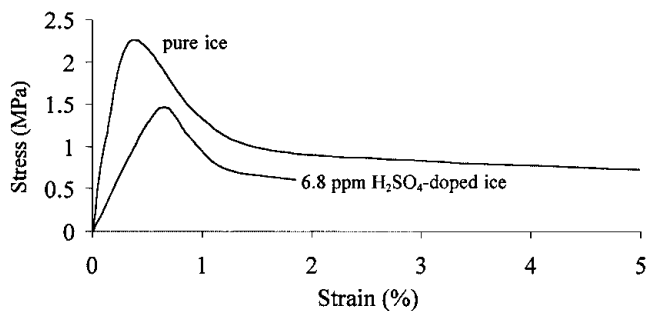
Fig. 7. Comparison between the engineering stress–strain curves at an axial strain rate of $1 \times 10^{-5} \, s^{-1}$ at $-20°C$ for pure ice and H_2SO_4-doped (6.8 ppm) ice single crystals with $\theta = 25°$.
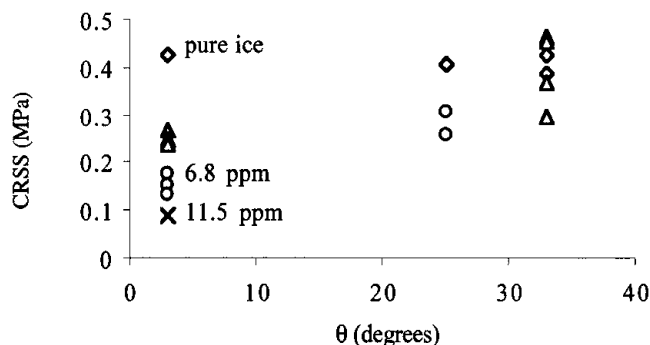

Fig. 8. Graph of the peak CRSS for pure ice and for H_2SO_4-doped ice with various dopant levels (indicated) and orientations at $-20°C$ normalized to a shear strain rate on the basal slip plane of $1 \times 10^{-5} \, s^{-1}$.

The softening mechanism of H_2SO_4 should be different from HF since SO_4^{2-} occurs as an interstitial ion in the lattice but F^- is present as a substitutional one. H_2SO_4 might increase the dislocation mobility due to the addition of two H^+ ions from each H_2SO_4 molecule. It also might be expected (see Introduction) that the H_2SO_4 doping would change the dislocation density. The latter possibility was investigated briefly using synchrotron X-ray topography.

Although all the specimens for the X-ray topography study appeared to be good single crystals as determined under
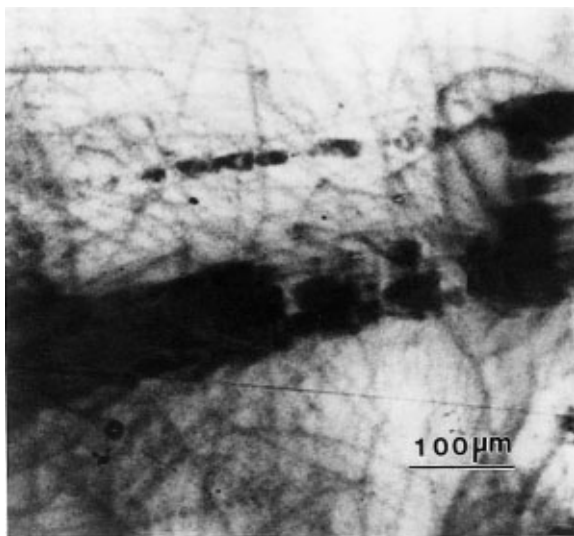

Fig. 9. X-ray topograph showing a sub-grain which satisfied the operating diffraction conditions in a specimen doped with 11 ppm of H_2SO_4. The dislocation density was estimated to be $> 1 \times 10^{10} \, m^{-2}$.

the polarized light, sub-grains were clearly present in the as-grown H_2SO_4-doped ice single crystals. Dislocations were observed only in the sub-grains that satisfy the operating diffraction conditions; other sub-grains appear black. If the diffraction conditions were changed, different sub-grains were in contrast. The dislocation density in these sub-grains was quite high (compared to previously observed dislocation structures in undoped crystals) at $> 1 \times 10^{10} \, m^{-2}$ (see Fig. 9). This observation of a high dislocation density in H_2SO_4-doped ice is similar to the observations of a greatly increased dislocation density in NH_3-, HCl- and HF-doped ice found by Jones and Gilra (1972) and Oguro (1988). Regarding this observed high dislocation density in doped ice, it is well to keep in mind that although our method for making X-ray topography specimens works well with pure ice, there is a possibility that the softening effects from acids (HF, HCl and H_2SO_4) make it easier for dislocations to be introduced into doped crystals during specimen preparation. However, it does appear that at least part of the softening effect from sulfuric-acid doping is due to the presence of a high dislocation density.

CONCLUSIONS

Single crystals of ice of various orientations containing various concentrations of H_2SO_4 up to 11.5 ppm were strained under compression, and the following conclusions were derived:

1. Both the CRSS (peak stress) and subsequent flow stress in ice single crystals are reduced by doping with sulfuric acid.

2. The peak CRSS of H_2SO_4-doped ice decreases as the square root of the concentration of H_2SO_4 increases.

3. The peak CRSS of H_2SO_4-doped ice single crystals depends on their crystallographic orientation, i.e. Schmid's law is not obeyed.

4. The addition of H_2SO_4 appears to increase the ductility of ice crystals.

5. The solubility limit of H_2SO_4 in ice single crystals is at least 11.5 ppm.

6. X-ray topography indicates that at least part of the softening effect from H_2SO_4 doping is due to a high grown-in dislocation density.

ACKNOWLEDGEMENTS

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