

## THE CREEP OF NaCl-DOPED ICE MONOCRYSTALS

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**ABSTRACT.** Monocrystals of ice grown from NaCl solutions (concentration  $5 \times 10^{-4}$  to  $10^{-2}$  mol/l) have been tested in creep at  $-10^{\circ}\text{C}$  by basal glide. The maximum resolved shear stress ranged from 0.6 to 2.5 bar. The resulting creep curves show a deceleration, that is, the creep rate decreases with time. At the highest concentration the creep is essentially transient; the strain tends to a fixed value. This is unlike the behaviour of similarly orientated monocrystals of pure ice or of ice grown from solutions of other dopants so far reported in the literature.

The possible causes for this behaviour are discussed and the implications for the mechanical properties of polycrystalline ice, and in particular sea ice and glacier ice, are described.

**RÉSUMÉ.** Fluage de monocristaux de glace dopée avec NaCl. Des monocristaux de glace obtenus par croissance à partir de solutions de NaCl (concentrations  $5 \times 10^{-4}$  à  $10^{-2}$  mol/l) ont subi des essais de fluage à  $-10^{\circ}\text{C}$ , le plan basal étant le plan de glissement. La valeur maximale de la contrainte réduite est comprise entre 0,6 et 2,5 bar. Les courbes de fluage obtenues montrent une décélération c'est-à-dire une diminution de la vitesse de déformation au cours du temps. Aux concentrations les plus élevées, il y a essentiellement un fluage transitoire: la déformation tend vers une valeur limite. Ce comportement est très différent de celui de monocristaux de même orientation de glace pure ou de glace dopée avec d'autres composés tel qu'il est indiqué dans la littérature.

Les origines possibles de ce comportement sont discutées et les explications quant aux propriétés mécaniques de la glace polycristalline (en particulier de la glace de mer ou de glacier) sont décrites.

**ZUSAMMENFASSUNG.** Das Kriechen von NaCl-dotierten Eis-Einkristallen. Eis-Einkristalle, die aus NaCl-Lösungen (Konzentration  $5 \times 10^{-4}$  bis  $10^{-2}$  mol/l) gezüchtet wurden, wurden im Kriechversuch bei  $-10^{\circ}\text{C}$  durch basale Gleitung verformt. Die maximale Schubspannung in der Gleitebene erstreckte sich von 0,6 bis 2,5 bar. Die gewonnenen Kriechkurven zeigen ein verzögertes Kriechen, d.h. die Kriechgeschwindigkeit nimmt mit der Zeit ab. Bei der höchsten Konzentration findet man im wesentlichen ein Übergangskriechverhalten; die Verformung strebt einem festen Wert zu. Dies ist vom bisher in der Literatur beschriebenen Verhalten ähnlich orientierter Einkristalle aus reinem Eis oder von Eis aus Lösungen anderer Dotierungsstoffe verschieden.

Die möglichen Ursachen für dieses Verhalten werden besprochen, und die Bedeutung für die mechanischen Eigenschaften von vielkristallinem Eis, im besonderen von Meereis und Gletschereis, wird beschrieben.

### INTRODUCTION

The creep of pure monocrystals of ice Ih orientated for basal glide has long been known to be accelerating, that is, the strain-rate increases with time since loading (Glen and Perutz, 1954). The corresponding deformation behaviour in a constant strain-rate test is: after an initial rise of stress with strain up to a maximum or upper yield stress  $\tau_{\text{max}}$ , the stress drops with continuing strain at a decreasing rate; the material work-softens (Weertman, 1973).

More recent work on doped ice by Jones and Glen (1969) with HF and  $\text{NH}_3$  dopants, Nakamura and Jones (1970) with HCl, and Nakamura and Jones (1973[a], [b]) with HCl, HBr,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{F}$ , NaF, KF, NaOH,  $\text{H}_2\text{O}_2$ , and He has shown that the same form of accelerating creep curve or strain-stress curve with yield drop is found with these dopants present. The main difference in behaviour from pure ice monocrystals, where any was observed, was a lower stress in the constant strain-rate tests and a steepening or flattening of the curves relative to pure ice; the doped material still work-softened. In this paper, however, results clearly different from the work reported above are presented for NaCl-doped ice: the creep shows a work-hardening effect.

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## METHOD

*Crystal manufacture*

The water used to prepare the NaCl solutions was deionized and had impurity levels  $F^- \leq 10^{-8}$  and  $Cl^- \leq 10^{-6}$  mol/l. The electrical conductivity originally  $< 10^{-5} \Omega^{-1} m^{-1}$  rose in contact with air to  $10^{-4} \Omega^{-1} m^{-1}$ . Water of the same purity was used for cleaning all glassware. The water was boiled to remove air and then cooled under reduced pressure before the dopant was introduced.

The dopant was prepared from analytical grade crystalline NaCl dissolved in the pure water to produce a series of standard solutions.

The crystals were grown, at  $-7^\circ C$ , by the method reported by Glen and Perutz (1954) in glass tubing. They were supported at an angle of  $45^\circ$  to the solution surface so that the  $c$ -axis of the resulting crystal was  $45^\circ$  from the cylinder axis, i.e. orientated for easy glide. The glass tubes had a nominal inside diameter of 3 mm and a nominal length of 80 mm. This gives long thin crystals with a ratio of gauge length to diameter well above six, the value recommended from normal tensile-testing practice. Growth took 2 d, so giving an average growth rate of  $0.5 \mu m s^{-1}$ .

*Testing and data reduction*

All crystals were examined visually for flaws and grain boundaries under normal illumination and between crossed polaroids; imperfect crystals were rejected. The  $c$ -axis orientation was determined optically before the crystals were mounted in the tensile-test machine, as used by Homer (unpublished). The crystals were subjected to a constant load and their elongation measured as a function of time by a displacement transducer (Sangamo Weston Controls Ltd., Miniature DC/DC Transducer Type DR/0.100). Its output voltage was displayed on a chart recorder.

The temperature was controlled by a Pt-resistance thermometer and an electronic temperature control unit (Fielden Electronics Ltd., Type Ti B 2) and kept within the range  $-10$  to  $-11^\circ C$ .

The tensile load and the resulting displacement were converted into maximum resolved shear stress  $\tau$  and maximum resolved shear strain  $\gamma$  in the basal plane, using the equations of Schmid and Boas (1950, p. 59) where necessary.

*Dopant concentrations*

In order to measure the ionic concentrations, the specimen was melted in  $5 cm^3$  of the pure water or else a sample of suitable size was prepared by melting ice which grew close to the tested sample. The  $Cl^-$  measurement used a  $Cl^-$ -ion electrode from Orion Research Inc., Model 94-17, in conjunction with the double-junction reference electrode, Model 90-02, and Specific Ion Meter, Model 401. This equipment gave good repeatability, any variation being of the order of 5%. The  $Na^+$  levels were difficult to determine. Flame photometry and atomic absorption spectrometry (using an Atomic Absorption Spectrophotometer Evans Electro-selenium EEL 240) gave a  $Na^+$  concentration of  $\leq 1.5 \times 10^{-6} M$ . The concentrations in the mother solution and those found in the crystal are given in Table I.

TABLE I. DOPANT CONCENTRATIONS IN THE MOTHER SOLUTION AND IN THE CRYSTALS

<i>NaCl concentration in the mother solution</i> mol/l	<i>Cl<sup>-</sup> concentration in the crystal</i> mol/l	<i>Na<sup>+</sup> concentration in the crystal</i> mol/l
$10^{-2}$	$(1.5-3.0) \times 10^{-3}$	$\leq 1.5 \times 10^{-6}$
$10^{-3}$	$(0.5-1.0) \times 10^{-5}$	$\leq 1.5 \times 10^{-6}$
$5 \times 10^{-4}$	$(1.5-2.5) \times 10^{-4}$	—

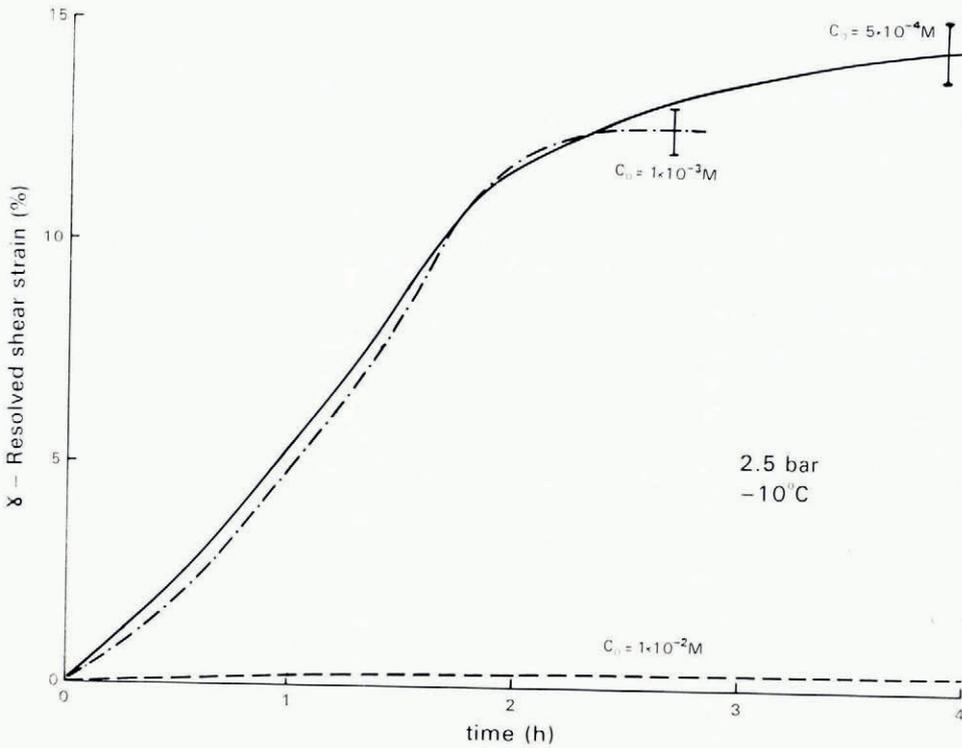


Fig. 1. Creep curves of ice monocrystals grown from NaCl solutions, concentration  $c_0$  of mother solution between  $5 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol/l, temperature  $-10^\circ\text{C}$ , maximum resolved shear stress  $\tau = 2.5$  bar.

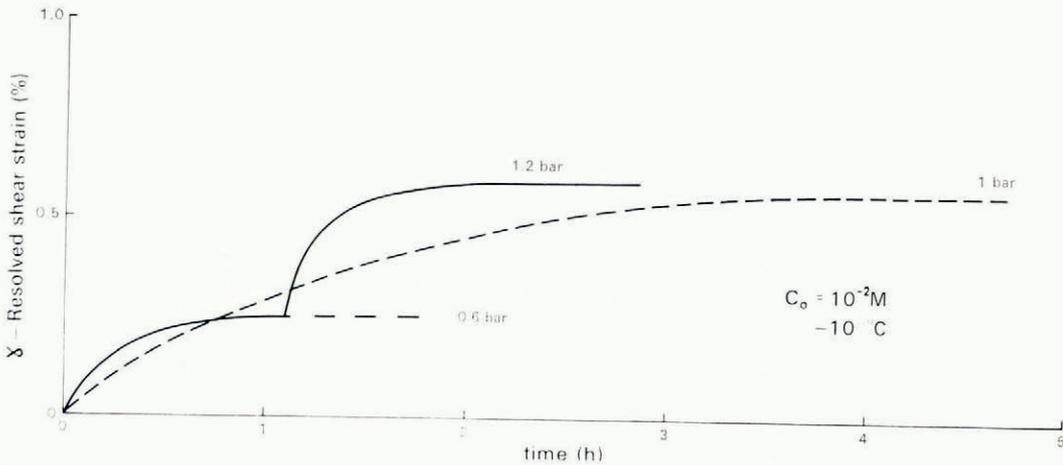


Fig. 2. Creep curves for ice monocrystals grown from NaCl solutions with concentration  $c_0$  of the mother solution  $10^{-2}$  mol/l. One crystal was loaded in two steps, the maximum resolved shear stress  $\tau$ , originally 0.6 bar, was increased after 1 h to 1.2 bar. The other crystal had a constant load for which  $\tau = 1$  bar.

## RESULTS

### *Creep curves*

The variation of the resolved basal shear strain with time for differing dopant concentrations and different loading sequences is shown in Figures 1 and 2. The general appearance of all these curves is of decelerating creep. The errors incurred in calculating the resolved strain, which are estimated at  $\leq 10\%$ , are such as to affect only the ordinate of the curves and not the sign of the curvature.

Figure 1 shows the shear strain over time for a range of dopant concentrations, the hardening effect being more marked at the higher concentrations. At the highest concentration the creep is essentially transient; the strain tends to a fixed value.

Figure 2 shows two different loading sequences. One crystal was first loaded so that the resolved shear stress  $\tau = 0.6$  bar. After its creep had stopped, the load was increased, bringing  $\tau$  to 1.2 bar. It then began to creep again but came to a final resolved shear strain very similar to that which one might expect for a direct loading of this magnitude in one step. For comparison a curve for  $\tau = 1$  bar is shown.

The apparatus was checked in various ways to exclude an experimental artefact. Pure monocrystals grown by the same method as the doped crystals and tested in the same test machine showed an accelerating creep.

## DISCUSSION

### *Incorporation of NaCl into ice*

The first point of importance is to establish which kinds of impurities and defects are introduced into the ice monocrystals when they grow from dilute aqueous NaCl solutions. As our chemical analyses are insufficient for this, a comparison with data from the literature may help. Maeno (1973) detected no  $K^+$  in monocrystals grown from KCl mother solutions with concentrations between  $10^{-5}$  and  $2 \times 10^{-3}$  mol/l; the  $Cl^-$  concentration in his monocrystals was a factor  $2 \times 10^{-2}$  to  $10^{-1}$  below that of the mother solution. According to G. W. Gross (personal communication during the Symposium), we may expect the  $Na^+$  concentration in our crystals to be more than one order of magnitude below the  $Cl^-$  concentration.

The freezing of KF and NaF solutions (Cobb and Gross, 1969) resulted in cation concentrations in ice smaller than those of the anion, the difference being greater at lower concentrations of the mother solution and at low freezing rates. "Chlorides of sodium and potassium showed similar trends in general to the fluorides, but at a given solution concentration the fraction incorporated into the ice was generally smaller for the chlorides" (Cobb and Gross, 1969, p. 800). Although the ice in these experiments was polycrystalline, we think that the above results may be applicable to our ice samples.

With  $Cl^-$  as the predominant solute in our ice crystals, we might expect our results to be similar to those obtained for HCl-doped ice monocrystals. Constant strain-rate tests on such crystals by Nakamura and Jones (1970, 1973[a], [b]) showed a yield drop like tests with other dopants. The HCl-doped crystals were even "softer" than pure ice in the sense that the stress required to maintain a constant strain-rate was smaller compared with pure ice, but this "softening" effect was less pronounced than it was for HF-doped crystals. These results do not agree even qualitatively with ours. As the work by Jones and Glen (1969) and Nakamura and Jones (1970, 1973[a], [b]) used the same method of crystal growth as the present work, we can feel reasonably sure that our result is not an artefact of growth technique.

Kuroiwa's (1964) measurements of the mechanical anelastic damping of polycrystalline ice grown from solutions of NaCl, NaOH, and HCl give further information about the effect of doping. The relaxation peak of the anelastic damping due to re-orientation of  $H_2O$  molecules, is influenced by the solute dispersed within the grains. But, whereas the behaviour of the

relaxation peak of the NaOH-doped ice is very close to that of a pure crystal, the HCl-doped crystal shows a large difference from pure ice. NaCl-doped ice lies in between but closer to the HCl-doped ice, the activation energy for these two types being the same. An additional anelastic damping peak appearing at low temperatures suggests that all three dopants can separate in the ice in the form of aggregates.

#### *Shape of the observed curves*

The shape of the creep curves for the NaCl-doped ice is similar to that for metals, for which the explanation given is that a large number of dislocations, created almost instantaneously after application of stress, interact with each other (Weertman, 1973). NaCl may increase the density of dislocations above the normally low level (relative to metals) found in ice because of the manner in which it is incorporated, or it may provide a mechanism for their more rapid generation. In both cases their interaction may result in a decelerating creep as in metals. Another possibility is that incorporated NaCl may form obstacles at which the existing dislocations are getting held up or pinned, thus decelerating the creep. One way of approaching a choice between these two mechanisms via creep-test data would be to observe the rate of change of creep on loading and compare this with the results from pure specimens. A consistently faster initial response from the doped material may well indicate a higher dislocation density than in the pure material. Conversely, if the effect is due to trapping of dislocations, we could expect the creep to be slower compared with pure crystals at their slowest. This is now being investigated.

A final point worth noting is that Harrison and Tiller (1963) have reported a cellular structure developing at the ice-water interface for NaCl solutions freezing at rates similar to those estimated here. Structures attributed to the same mechanism as that identified by Harrison and Tiller have been well shown by scanning electron-microscope micrographs, produced by Sinha (1977), of the internal structure of sea-ice crystals (in which the salt concentrations are two to three orders of magnitude greater than in the crystals we have tested). It may well be that such a structure still exists at our concentrations and so acts as obstacles to dislocation movement. Unfortunately, Harrison and Tiller's work did not include any of the dopants that we know to give an accelerating creep curve.

It is probable that we will have a lattice-impurity content throughout the crystal as well as any internal structure. Paren and Walker (1971) have estimated the solubility limit for sea salts in cold ice to be  $2 \times 10^{-6}$  mol/l. If this is valid, then it may be that the change in hardening effect between the different curves of Figure 1 shows the increasing effect of the internal structures.

#### *Implications for polycrystalline ice*

Barnes and others (1971) discussed the contributions made by creep, surface regelation, and grain-boundary processes in resisting indentation of the surface of pure polycrystalline ice in the pressure-melting regime. Over the range of loads 10–190 bar and loading times  $10^{+4}$  to  $10^{-4}$  s, they estimated the contribution from creep to range between 30 and 40%. In a polycrystalline NaCl-doped ice we might, following our results, expect the creep component to be reduced as hardening progresses and so the proportion to be borne by the other processes would increase.

#### *Glacier ice*

The bulk NaCl content of temperate glaciers is probably below the minimum tested here. Although Lliboutry (1971) gave a range of  $10^{-3}$  to  $10^{-4}$  mol/l for concentrations in falling snow, Souchez and others (1973) found bulk concentrations of  $\text{Na}^+$  from  $4.3 \times 10^{-6}$  to  $12 \times 10^{-6}$  mol/l for basal ice of Glacier d'Argentière, and Harrison and Raymond (1976) gave an estimated value of  $0.7 \times 10^{-6}$  mol/l for the lattice impurity for all salts in Blue Glacier.

As we expect almost all the impurities to have migrated to the grain boundaries (Kuroiwa, 1964), the intragranular concentrations will be less than these bulk values. This would mean that the NaCl contribution to the monocrystal creep behaviour would be less than that shown by the upper curve of Figure 1, but it remains possible that even this low concentration might modify the behaviour from that of pure ice, and the effect could well be more important in polar glaciers where migration to grain boundaries is impeded.

#### Sea ice

Sea ice consists of polycrystalline ice with salts, mainly NaCl, included in pockets. According to our measurements, the creep of the ice grains may be expected to be quite different from that of pure ice, so that the mechanical properties of sea ice could not be treated theoretically by assuming it to be a system of pure ice with salt or brine inclusions. The properties of the ice phase in sea ice should be investigated but the present results give us a strong indication of what might be found.

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## DISCUSSION

J. KLINGER: I wonder about the relatively high NaCl concentration in your samples; how did you grow them?

N. W. RILEY: Crystals were grown from an NaCl mother solution of  $10^{-2}$  to  $5 \times 10^{-4}$  mol l<sup>-1</sup> in glass tubes by the Glen method at a temperature of  $-7^{\circ}\text{C}$ , the average rate of growth being  $0.5 \mu\text{m s}^{-1}$ .

KLINGER: Did you do any pH measurements in the mother solution during growth? This would be a good test to see if there is any preferential incorporation of Na<sup>+</sup> or Cl<sup>-</sup> ions into the crystal.

RILEY: pH measurements were not made in the mother solution. The dopant concentrations in the tested crystals were found by melting the crystals and measuring Cl<sup>-</sup> concentration by specific-ion electrode. We attempted to determine the Na<sup>+</sup> concentration by additional conductivity measurements, by flame photometry and atomic absorption spectrometry. But all this produced nothing definite, perhaps because of the very strong rejection of Na<sup>+</sup> reported at this symposium by Dr Gross.

G. NOLL [written contribution]: Direct pH measurements in the mother solution during growth would introduce electrolyte from the reference electrode and therefore interfere with the growth of doped crystals. We have made pH measurements of melted NaCl-doped ice. The sum of the Na<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> concentrations in these samples matched the Cl<sup>-</sup> concentrations within the experimental error.

J. PEREZ: There is a difficulty in understanding the role of doping agents, which depends on whether they are in solid solution or not. Do you not think that NaCl may form some sort of microscopic precipitates which should be obstacles to dislocation glide?

RILEY: Yes, precipitates could be present; if they were, then they would be potential obstacles. But the observations of Dr Gross seem to decrease the probability of this because of the strong Na<sup>+</sup> rejection.

The type of obstacle reported by Harrison and Tiller (1963) may be more likely. Perhaps a way of determining whether these obstacles are present or not and their type is to use the technique described by Sinha (1977) for replicating sea-ice brine cells for examination by scanning electron micrographs.

G. W. GROSS: When freezing is slow, NaCl in dilute solution (such as used in this work) is equivalent to HCl because most of the sodium (99%) is rejected into the liquid. The distribution coefficient of the chloride (in sodium chloride) is about  $2 \times 10^{-3}$ , that is, a fraction of  $2 \times 10^{-3}$  times the concentration in the liquid adjacent to the interface is incorporated into the solid. As a result, a high-concentration boundary layer forms in the liquid adjacent to the interface (about two orders of magnitude above the original concentration of the mother solution). This is lowered somewhat by convection about the  $4^{\circ}\text{C}$  isotherm. If this concentration exceeds a critical value, it leads to interface break-down and the cellular structure described by Harrison and Tiller (1963).