Pressure-Induced Transformation Plasticity of H_2O Ice

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Transformation plasticity is a deformation mechanism which occurs during phase transformation of an externally stressed material. Pressure-induced transformation plasticity of ice could be relevant to the geology of the moons of the outer solar system, and has long been postulated to occur in olivine in the earth's interior. In the present work, ice specimens were subjected to isostatic pressure cycling between 0 and 300 MPa to induce reversible polymorphic transformation between ice I and II at 230 K. When a small uniaxial compressive stress was applied during cycling, the specimens exhibited a compressive strain (as large as 18.5% after a single cycle) proportional to the applied stress, in agreement with observations and theory for transformation plasticity of metals induced by polymorphic thermal cycling.

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The high pressure polymorphs of ice are believed to exist in the interior of many of the icy satellites of the outer planets [1,2]. Because of its relevance to the tectonics of these moons, the rheology of ice polymorphs has been extensively studied, as reviewed recently in Ref. [3]. While creep by dislocation motion and grain-boundary sliding have been measured in coarse- and fine-grained ice polymorphs under isobaric and isothermal conditions, there has been to date no experimental demonstration of transformation-mismatch plasticity in ice produced by a change in isostatic pressure and/or temperature. Transformation-mismatch plasticity (referred to as *transformation plasticity* in the present article) occurs when a polymorphic material undergoes a phase transformation while being subjected to a small deviatoric stress [4,5]. During the transformation, the mismatch in density between the coexisting polymorphic phases produces internal stresses. If no external stress is applied on a transforming specimen, these internal stresses give rise to plastic strains which are accumulated isotropically after the forward phase transformation (e.g., upon heating), but which are completely recovered after the reverse phase transformation (e.g., upon cooling). However, if an external deviatoric stress is applied to the specimen during the phase transformation, this stress biases the internal strains, resulting in a net strain increment in the direction of the deviatoric stress after each phase transformation (e.g., both upon heating and cooling). This deformation mechanism has been extensively studied in a variety of polymorphic metals, alloys, and ceramics [4,5] subjected to thermal cycling about their transformation temperature at constant, atmospheric pressure. Strain increments produced after each thermal cycle can be accumulated, leading to very high elongations to fracture (superplastic tensile strains larger than 100% are commonly achieved in metals and alloys [4,5]). Transformation plasticity is also widely acknowledged to be a relevant deformation mechanism within the earth's mantle through the pressure-induced transformation of olivine [6,7]. However, transformation plasticity produced by pressure variations has, to our knowledge, never been observed experimentally in any material.

Figure 1 shows a section of the H_2O phase diagram with equilibrium and metastable boundaries between fields for ice I, II, III, and V [3]. The maximum pressure in the largest icy moons of the outer solar system is expected to be well within the high-pressure polymorphic fields [1]. Then, as for olivine within Earth's mantle, there should be a critical depth in these moons where transformation plasticity of ice can be an active deformation mechanism. While the gravitational isostatic pressure in these moons is sufficient to trigger the ice polymorphic transformations, deviatoric stresses can be provided by, e.g., mantle convection, hot plumes, faulting, tidal and spin forces, or meteoritic impact.

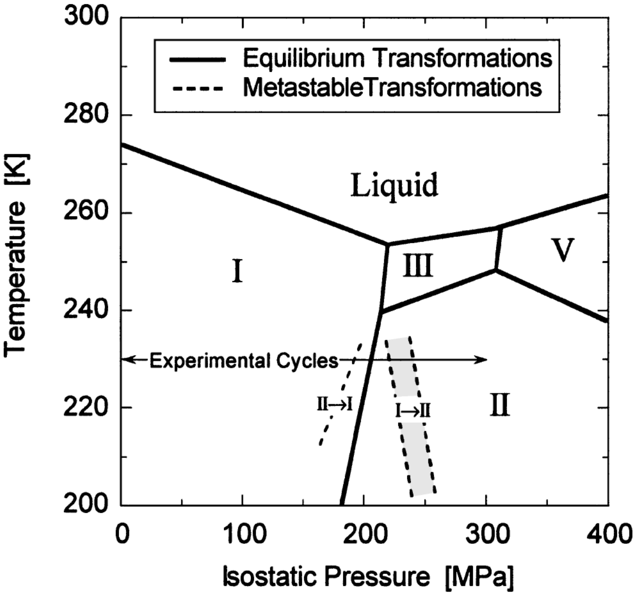

FIG. 1. Section of H_2O phase diagram showing equilibrium and metastable boundaries between fields for ice I, II, III, and V (3), as well as the range of experimental pressure cycles.

Then, large strains could be produced in the ice layer at the critical depth, leading to a rheologically weak region which can influence the global tectonics of these moons. In this report, we describe experiments which demonstrate transformation plasticity for pure ice subjected to isothermal pressure cycling between ice I and II, while simultaneously experiencing a small uniaxial compressive stress.

Ice powders were produced by atomizing deionized water into liquid nitrogen and sieving to $<25\ \mu$m. The powders were vacuum hot pressed for 2 h at 190 K under a uniaxial pressure of 100 MPa. These fabrication procedures have been shown to produce fully dense ice with a grain size of 25–40 μm [8]. Following Ref. [9], cylindrical specimens 12.7 mm in diameter and 24–27 mm in length were introduced into thin-walled (150 μm) indium tubes which were sealed at both ends by soldering the indium jacket to copper-coated steel end caps [Fig. 2(a)]. An alumina plug was inserted between one end cap and the ice cylinder, the ends of which were covered with a 25 μm layer of Teflon to minimize friction during deformation. The indium jacket prevented gas penetration into the ice during pressurization, while accommodating the specimen deformation by creep with a negligible constraining force at the test temperatures.

Using a cryogenic pressure vessel [10] with nitrogen as a pressure medium, jacketed specimens were first subjected to an isostatic pressure cycle up to $p_{\mathrm{iso}} = 200$ MPa (within the field of ice I) at the test temperature of 230 or 240 K for 1 min, so as to eliminate any deformation due to porosity closure or settling of the specimen assembly. The length of the specimen assembly (typically 64–70 mm) was measured with a micrometer to $\pm 5\ \mu$m. The assembly was then introduced into a steel tube and spring loaded in uniaxial compression in the range $\sigma = 0 - 2.5$ MPa, using steel platens and steel springs calibrated at the test temperature. The compressively stressed specimen was placed in the pressure vessel and allowed to thermally equilibrate for about 10 min to 230 K, pressurized with nitrogen at an average rate of 1 MPa/s up to $p_{\mathrm{iso}} = 300$ MPa (within the metastable field of ice II at 230 K, Fig. 1), held at this pressure for 60 s, and finally depressurized at an average rate of 1 MPa/s. The length of the deformed, jacketed specimen assembly was again measured, and all deformation was assigned to the ice specimen. In some cases, a specimen was subjected to a second pressure cycle, and in one case ($\sigma = 1.38$ MPa) the test temperature was lowered to 220 K. Finally, two control experiments were conducted under compressive stresses of $\sigma = 0$ and 2.1 MPa at 230 K by cycling to $p_{\mathrm{iso}} = 200$ MPa (within the field of ice I) for the same total time as the transformation experiments.

The control specimens cycled within the field of ice I without phase transformation showed no measurable compressive strain for $\sigma = 0$ MPa and a small strain of 0.4% for $\sigma = 2.1$ MPa. Since ice II creeps at a rate lower than ice I [3], these control experiments show that deformation accumulated by creep outside the transformation range can be neglected for all I-II cycles.

The specimen volume change due to the ice I-II transformation at 230 K was recorded as a small, rapid (<1 s) gas pressure drop at $p_{\mathrm{iso}} = 257 \pm 5$ MPa on pressurization and a small, equally rapid pressure rise at $p_{\mathrm{iso}} = 195 \pm 3$ MPa on depressurization. For both transformations, these critical pressures are in good agreement with the metastable values given in Ref. [3] (Fig. 1) and confirm the nature of the polymorph produced.

After a single transformation cycle, the specimens were deformed to true compressive strains as large as 18.5%. Figure 2(b) shows a deformed specimen assembly: the ice specimen cross section has increased due to the uniaxial compressive strain, which was not completely uniform. The specimens were also usually somewhat barreled despite Teflon lubrication at the ends, but very rarely contained macrocracks. Also, the specimens were optically clear, indicating that microcracking was not extensive (or had been eliminated during the depressurization step by solid-state welding). All of these effects are expected to produce errors in the strain measurement, which are, however, still relatively small compared to the very large strains measured.

Figure 3 shows the uniaxial compressive strain after a single I-II cycle at 230 K as a function of the uniaxial

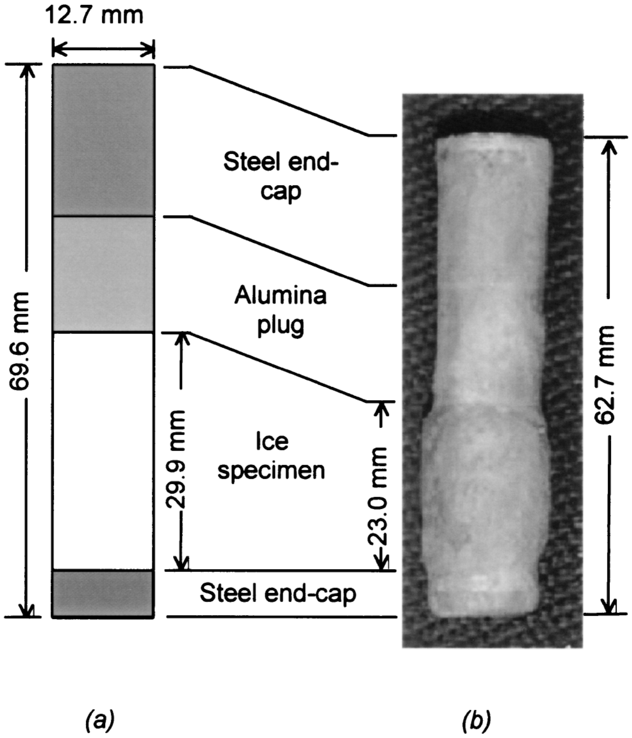

FIG. 2. (a) Schematic of typical specimen assembly before deformation. (b) Photograph of the same assembly showing axial and radial strains for an ice specimen after two I-II pressure cycles ($p_{\mathrm{iso}} =$ 0-300-0 MPa at 230 K) under uniaxial compressive stress $\sigma = 2.1$ and 1.5 MPa, respectively.

compressive stress. The linear relationship shown in Fig. 3 is strong evidence that transformation plasticity is the active deformation mechanism, as this linear relationship has been observed in all materials deforming by thermally induced transformation plasticity and is incompatible with the power laws expected for grain-boundary sliding [8] or dislocation creep [3]. Other indications for transformation plasticity are the high strains achieved after transformation cycling (much larger than the value of 0.4% for a control specimen cycled at $\sigma = 2.1$ MPa without phase transformation), and the absence of temperature sensitivity for an experiment performed at 220 K (the dislocation creep rate of ice I would be quadrupled from 220 to 230 K [3]; the grain-boundary sliding creep rate would be tripled [8]).

Greenwood and Johnson [11] developed a widely used relationship for the strain increment $\Delta\varepsilon$ accumulated after a full polymorphic cycle (forward and backward transformations), for the case where the weaker phase deforms by time-independent yield:

$$\Delta\varepsilon = \frac{5}{3}\,\frac{\Delta V}{V}\,\frac{\sigma}{\sigma_y}\,, \tag{1}$$

where $\Delta V/V$ is the magnitude of the volume difference between the two polymorphic phases and σ_y is the uniaxial yield stress of the plastically deforming, weaker phase (ice I in the present case [3]). Because of the speed of transformation (<1 s), it is appropriate to assume that deformation occurs by time-independent yield, not by time-dependent creep. Linear least-squares fitting of the data in Fig. 3 gives $\Delta\varepsilon/\sigma = 58\ \mathrm{GPa}^{-1}$, from which a yield stress $\sigma_y = 6.9$ MPa is calculated with Eq. (1) using $\Delta V/V = 24\%$ [3]. While there are no experimental data for the yield stress of ice near the transformation isostatic pressure, dislocation glide must occur at stresses above those for which creep is active: a creep strength of $\sigma = 59$ MPa is predicted for a strain rate of $0.1\ \mathrm{s}^{-1}$ at 230 K and $p_{\mathrm{iso}} = 228$ MPa [3]. Alternative deformation mechanisms with lower flow stresses may, however, be active: They include cracking (ice was found to crack in compression at $\sigma = 6.2$ MPa under rapid loading conditions at 233 K and atmospheric pressure [12]), dynamic recrystallization (particularly likely to occur during and just after the phase transformation), or biasing of the transformation strains due to the external stress (as discussed below).

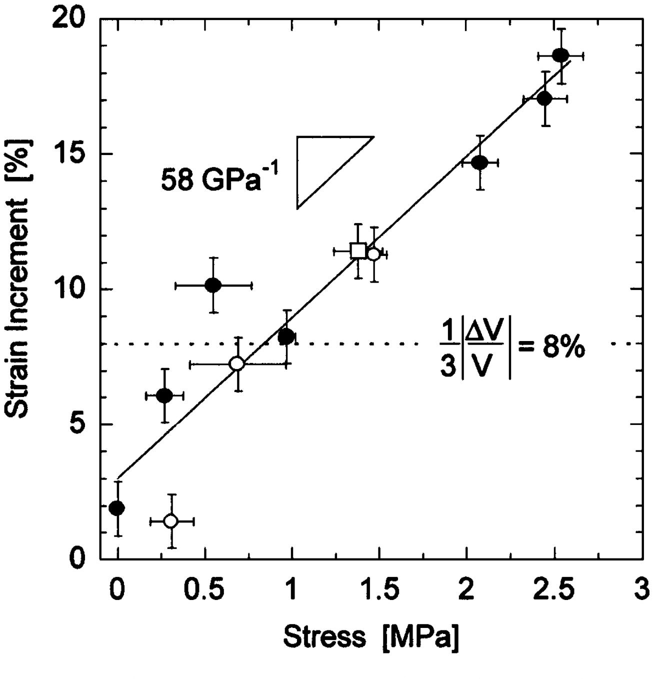

FIG. 3. Uniaxial compressive true strain as a function of uniaxial compressive true stress (both shown as positive values) after a single I-II polymorphic pressure cycle ($p_{\mathrm{iso}} = $ 0-300-0 MPa). Empty symbols are for specimens which has been subjected to a previous polymorphic cycle. The square symbol was measured at 220 K; all other points were measured at 230 K. Also shown for comparison is the reversible polymorphic uniaxial strain associated with each transformation (half-cycle).

The nonzero strain measured after pressure cycling for $\sigma = 0$ MPa in Fig. 3 indicates that *strain ratchetting* occurs upon pressure-induced transformation. This observation is similar to those reported in metals after temperature-induced transformation [13,14]. Possible causes for ice ratchetting include: (i) crystallographic texture produced by uniaxial hot pressing of the specimens, (ii) propagation of a transformation front; and (iii) a small amount of transformation plasticity due to deviatoric stresses developed by constraints at the ends of the specimen.

Whereas the present study examined isothermal transformation plasticity associated with the I-II transformation induced by isothermal pressure cycling, this deformation mechanism is expected for any transformation permitted by the H_2O phase diagram, i.e., under isobaric temperature variations (e.g., from ice II to III), or with simultaneous changes of both temperature and pressure along planetary profiles. For the largest icy moons of the outer solar system where isostatic pressures are sufficient to form ice isomorphs, many geological processes may be affected by transformation plasticity of the ice lithosphere: during the formation and early evolution of the moons (accretion and differentiation dynamics, solidification of an early global ocean) and for ongoing ice tectonics at the global scale (e.g., solid-state convection, spin and tidal bulging, coupling between rocky core and icy lithosphere). As reviewed in Ref. [15], the presence of a low-viscosity layer of creeping ice or liquid water can explain many small-scale geological features on Europa: thermal plumes, faulting, spreading centers, diapirism, topographic flexing around massifs, cryovolcanism, and formation and relaxation of surface features such as impact craters, cracks, and ridges. Transformation plasticity was not explicitly considered in Ref. [15] and could provide a low-viscosity layer in Europa and other large icy moons. Also, since the rheology of Europa's ice lithosphere controls both heat dissipation (by convection) and heat creation (by tidal deformation) [15], transformation plasticity may have important implications for the presence of a subsurface ocean on Europa.

Finally, our observations of pressure-induced transformation plasticity in ice can shed light on other geological materials for which pressure-induced transformation plasticity cannot be reproduced experimentally in the laboratory: olivine (e.g., in the mantle of rocky planets), iron (e.g., in large meteorites and the cores of planetesimals or some rocky moons), and solid hydrogen (e.g., in the core of giant planets).

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[1] J. P. Poirier, Nature (London) **299**, 683–688 (1982).
[2] C. Sotin, O. Grasset, and S. Beauchesne, in *Solar System Ices,* edited by B. Schmitt *et al.* (Kluwer Academic, Dordrecht, 1998), pp. 79–96.
[3] W. B. Durham, S. H. Kirby, and L. A. Stern, J. Geophys. Res. **102**, 16 293–16 302 (1997).
[4] J.-P. Poirier, *Creep of Crystals* (Cambridge University Press, Cambridge, 1985).
[5] T. G. Nieh, J. Wadsworth, and O. D. Sherby, *Superplasticity in Metals and Ceramics* (Cambridge University Press, Cambridge, 1997).
[6] H. W. Green and P. C. Burnley, Nature (London) **341**, 733–737 (1989).
[7] S. H. Kirby, W. B. Durham, and L. A. Stern, Science **252**, 216–225 (1991).
[8] D. L. Goldsby and D. L. Kohlstedt, Scr. Mater. **37**, 1399–1406 (1997).
[9] L. A. Stern, W. B. Durham, and S. H. Kirby, J. Geophys. Res. **102**, 5313–5325 (1997).
[10] W. B. Durham, H. C. Heard, and S. H. Kirby, J. Geophys. Res. **88**, B377–B392 (1983).
[11] G. W. Greenwood and R. H. Johnson, Proc. R. Soc. London **283A**, 403–422 (1965).
[12] P. V. Hobbs, *Ice Physics* (Clarendon Press, Oxford, 1974).
[13] J. J. Stobo, J. Nucl. Mater. **2**, 97–109 (1960).
[14] N. Furushiro, H. Kuramoto, Y. Takayama, and S. Hori, Trans. ISIJ **27**, 725–729 (1987).
[15] R. T. Pappalardo *et al.,* J. Geophys. Res. **104**, 24015–24055 (1999).