Microstructural Changes and Deformation during the Phase Transformations in Solid Ammonium Nitrate

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Abstract

Movie images were recorded with a polarised light microscope to examine the grain structures of a material undergoing phase transformations. The material, ammonium nitrate, was chosen simply because it has four stable crystal forms at temperatures below 170ºC, and not because it is a direct analog of any rock forming mineral. Thin films of the material were made by melting small dry crystals between glass slides then solidifying. Displacive and reconstructive phase transformations were observed directly using polarised light with the ammonium nitrate heated to appropriate transformation temperatures. Reverse transformations were observed by cooling. Since the heater was a few centimetres from the parts of the specimen being viewed, thermal gradients existed and in addition some time was needed for temperatures to rise- both of these allowed the phase transformations to be recorded as they passed through the field of view. For the transformations between different phases, there was seen a range from slow migration of cuspate phase boundaries to 'martensitic' shear transformation involving near-instantaneous formation of very narrow lenses of the new phase. In some cases shear stress was applied using a modification of the well known FUTRON^{TM} in-situ deformation apparatus and the stress was found to influence the transformation behaviour in a variety of ways. This type of analog approach, inspired by the pioneering work of Means in other systems, demonstrates some of the many ways that phase transformation and deformation processes could be interacting in response to stresses and to P, T, X, ... changes in the Earth and in our laboratories.

Introduction

Between room temperature and its melting point (169°C), ammonium nitrate exhibits four stable forms, designated IV, III, II, and I, respectively (Brown and McLaren, 1962). For the temperature ranges over which each of these forms are stable at atmospheric pressure, see the accompanying plot of specific volume as a function of temperature (Fig. 1). The sample configurations are shown in Figure 2 and Figure 3.
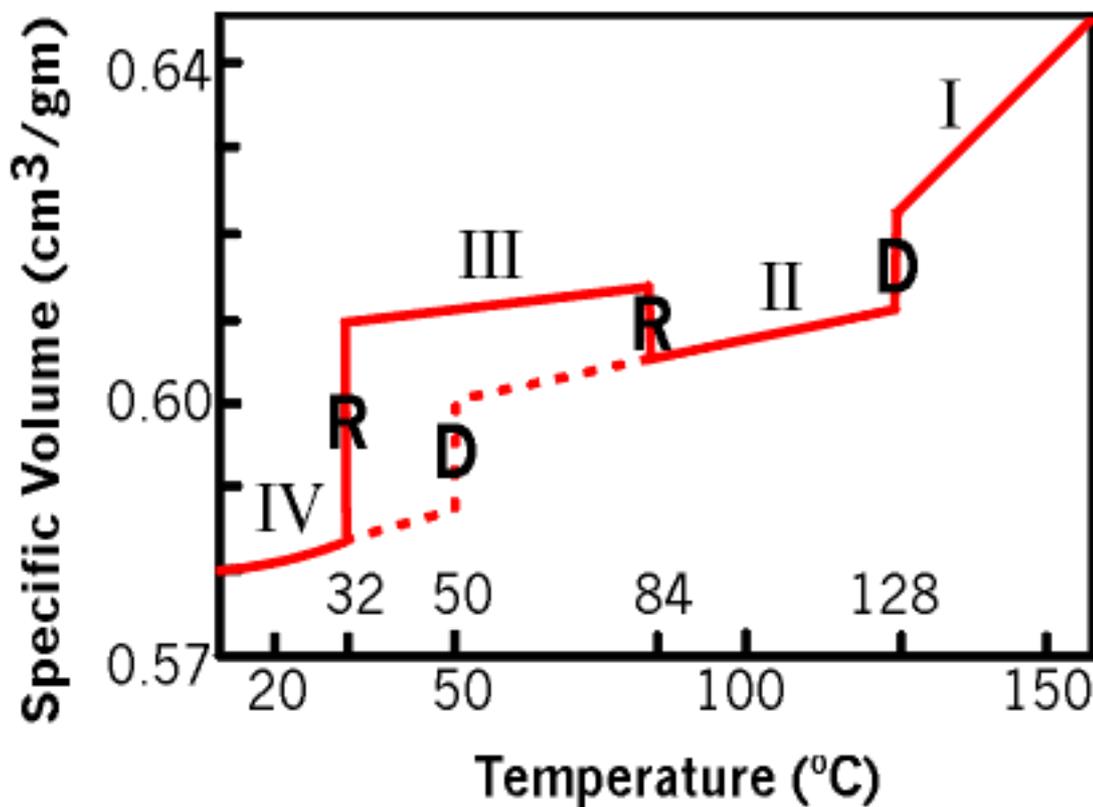
Figure 1. Phase Diagram – Specific Volume vs. temperature characteristics of the phases I, II, III and IV. Note the volume changes in the range ca. 1 % to 5 % at the first-order transitions. Transformations are labeled as being either displacive (D) or reconstructive (R).

Experiment Mounted on the Stage of a Light Microscope

Light Source

Transforming Specimen

Glass Slides

Heaters
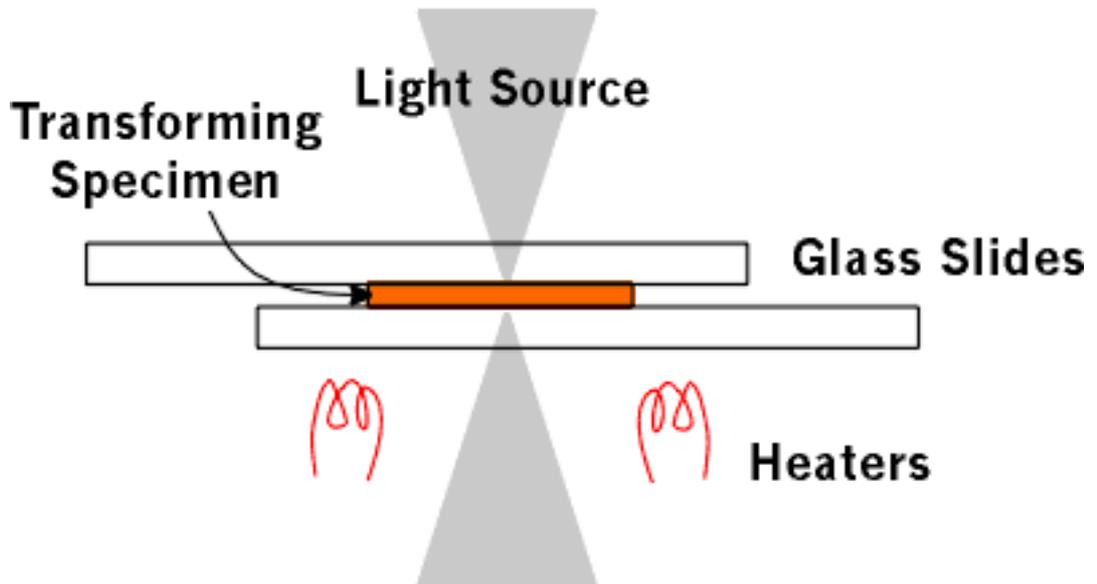
(Observations under crossed polarisers)

Figure 2. Experimental set-up for system with no external stresses applied.

Application of Stress

Light Source

Transforming Specimen

Glass Slides

Heaters

M
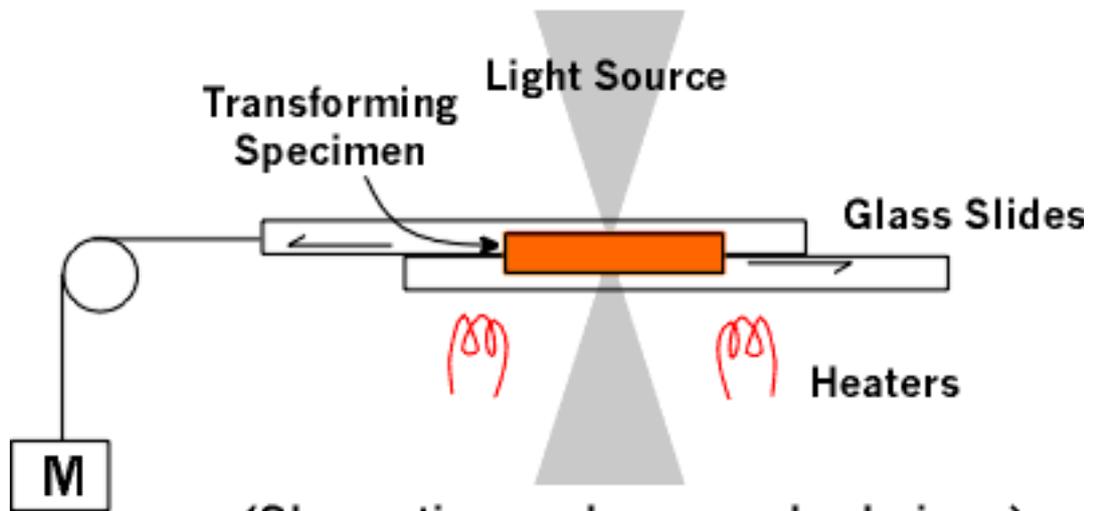
(Observations under crossed polarisers)

Figure 3. Experimental set-up for system with a constant stress applied.

Phase Transformations in the Absence of an Externally Applied Stress

Form IV (distorted CsCl structure) and form III (NiAs structure type?) are both orthorhombic and the transformation between these forms are reconstructive. Proton magnetic resonance (PMR) studies indicate that, at room temperature and above, the NH_4 ions are undergoing random reorientations, while X-ray studies indicate that the NO_3 ions are in fixed orientations only in forms IV and III. On heating III transforms to II which is tetragonal and structurally similar to IV: consequently the III to II transformation is also reconstructive.

Fig. 4 Single crystal of Phase IV transforms on heating at about 32°C into phase III. A 'faceted' interface advances slowly but steadily from the bottom left corner.
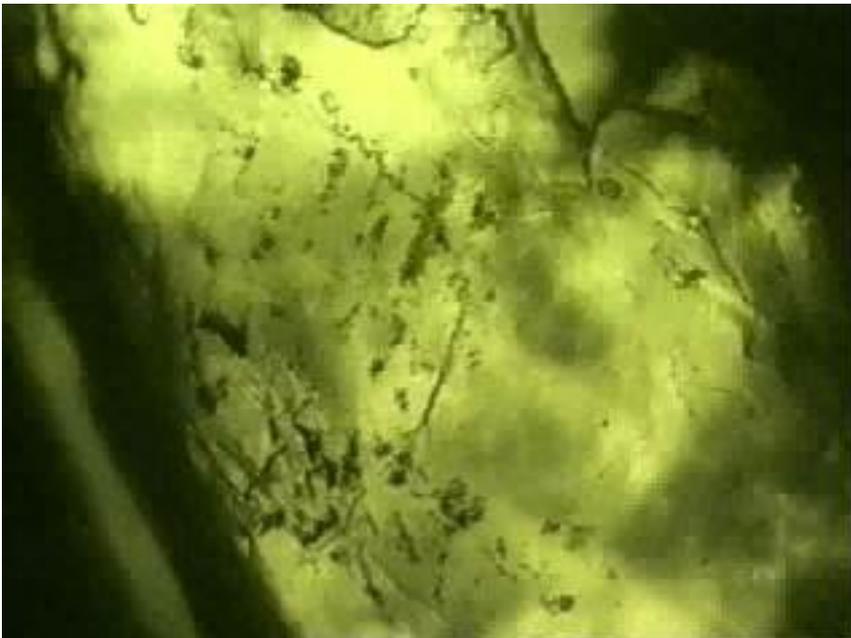
Fig. 5 Transformation to III is now complete. Rotation of the specimen in the movie (crossed polarisers) shows it is an extremely fine-grained polycrystal..
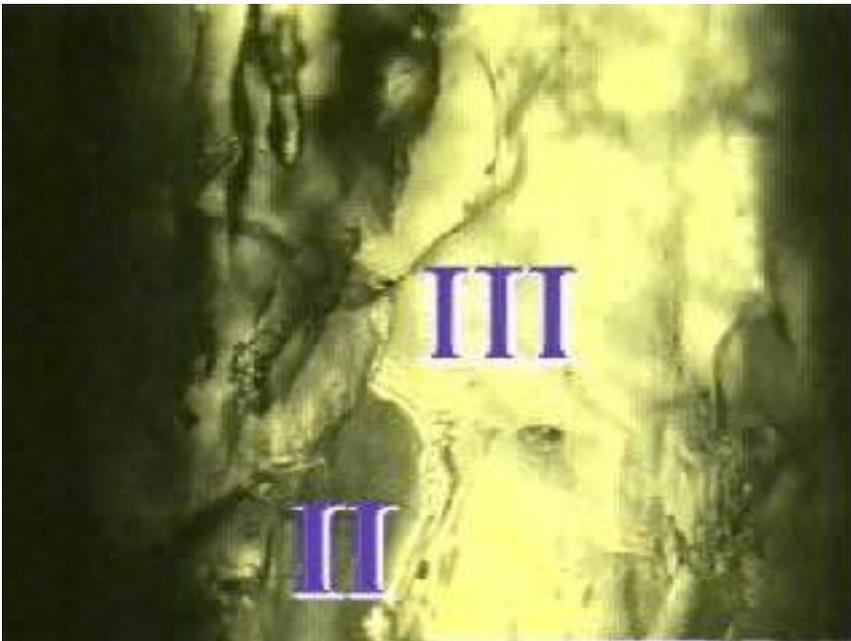
Fig. 6 III transforms on heating at ~85°C to II. The movie shows an interface which has a complex shape and which advances from south to north.
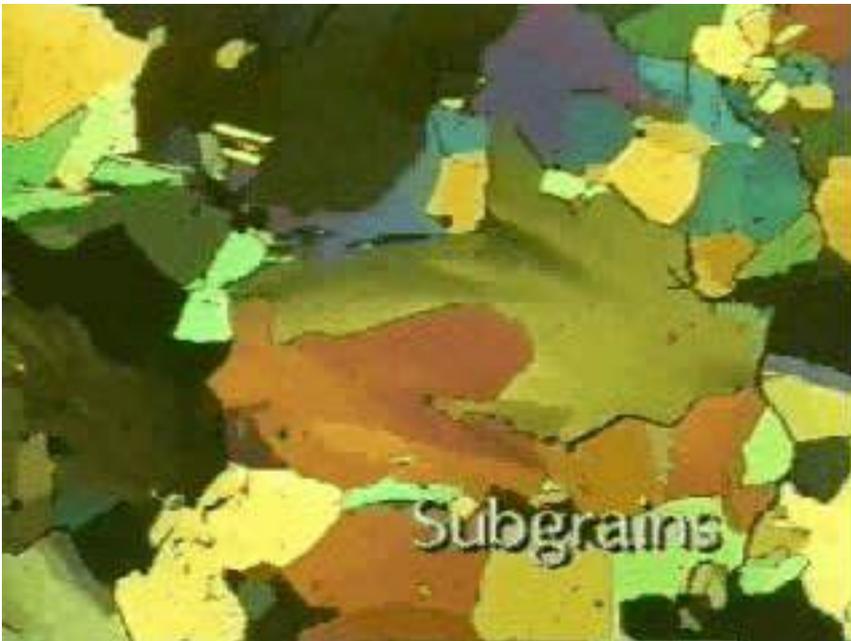
Fig. 7 Phase II cooled quickly from melt (via phase I). Contrasting colours represent crystals of different orientations- this preparation route is ideal for experiments needing polycrstalline aggregates. The movie contains a sequence where several regions of the polycrystal are rotated between crossed polarisers - elongate subgrains exist inside many of the larger grains.

Fig. 8 In this movie the II-I phase boundary moves in response to heating and cooling. The first temperature change is heating and the mobile phase boundary takes on cuspate shapes indicating some local pinning. The polarisers here are slightly uncrossed so that bubbles, etc in the cubic phase I are visible. Note that this is a solid state transition, not melting. The last part of the movie shows cooling where the grains of phase II enlarge mainly by epitaxial
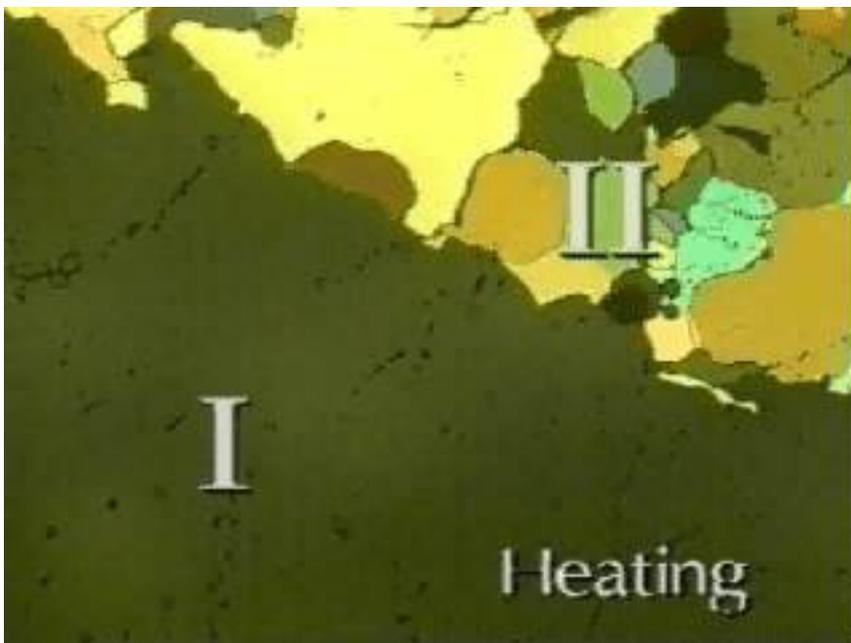
growth of those grains that originally touched the I-II boundary. This leaves large columnar grains of II behind the southward-moving boundary.

In form II the NO_3 ions are undergoing rotational disorder in their plane and electrical conductivity and PMR studies indicate the NH_4 ions are diffusing relatively freely compared with forms IV and III. However, the II to I transformation is displacive and the rotational disorder of the NO_3 ions in form I is no longer restricted to the plane of the ion. Thus both ions in I are essentially spherically symmetric and, consequently, I is cubic with the CsC1 structure. PMR evidence indicated a further, very significant, increase in the diffusion of the NH_4 ions at the II to I transformation, so that form I behaves like a superionic conductor. Forms II and IV are simply slight distortions of form I, brought about essentially by increasing rotational and/or translational order on cooling. The reconstructive transformations into III from either II (on cooling) or IV (on heating) occur only if some solvent for NH_4NO_3 is present, even in very small amounts. In perfectly dry specimens displacive transformations between IV, II and I only occur.

Although NH_4NO_3 is not a structural analogue of any important rock-forming mineral, it is, however, a very suitable material for studying the microstructural changes that take place during different types of solid-state phase transformations. The microstructural changes have been observed in thin films in the light microscope. Being reconstructive, the transformations involving form III usually lead to a significant reduction in grain size (Fig 5). However, the "massive" transformations between II and I lead to significant grain growth. The II to IV transformation is "martensitic" – small lenses of IV propagate rapidly across large grains of II, and then thicken steadily until all of the host grain is consumed (Fig 9).
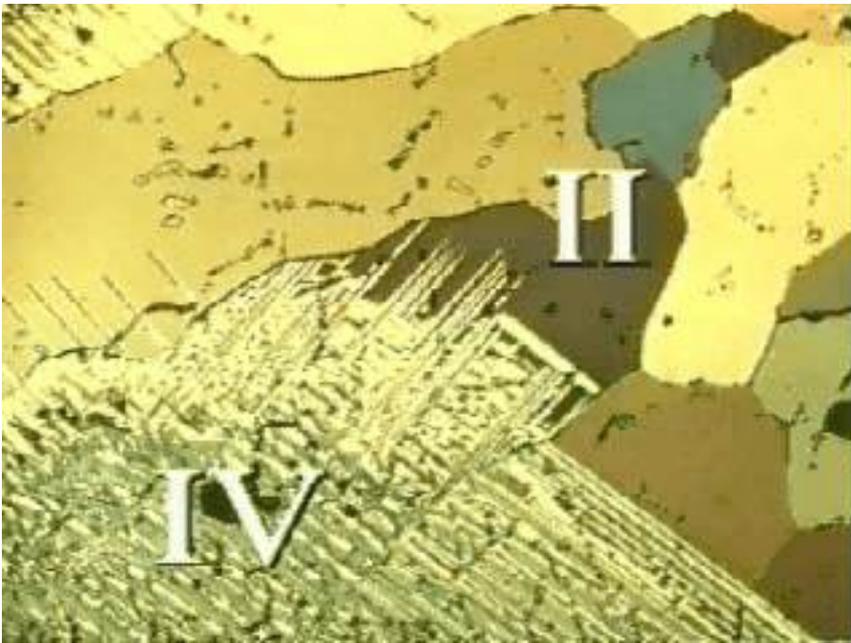
Fig. 9 Transformation of II to IV on cooling through ~50°C. "Martensitic"- rapid but sporadic. In the movie sequence a remarkable series of banded microstructures reveal how this type of shear transformation proceeds. Crystallographically controlled but narrow lenses of phase IV initiate then expand through each crystal of II. In some regions the advance of the lenses is steady, other regions show "instantaneous" conversion. There must be local internal stresses influencing this process.
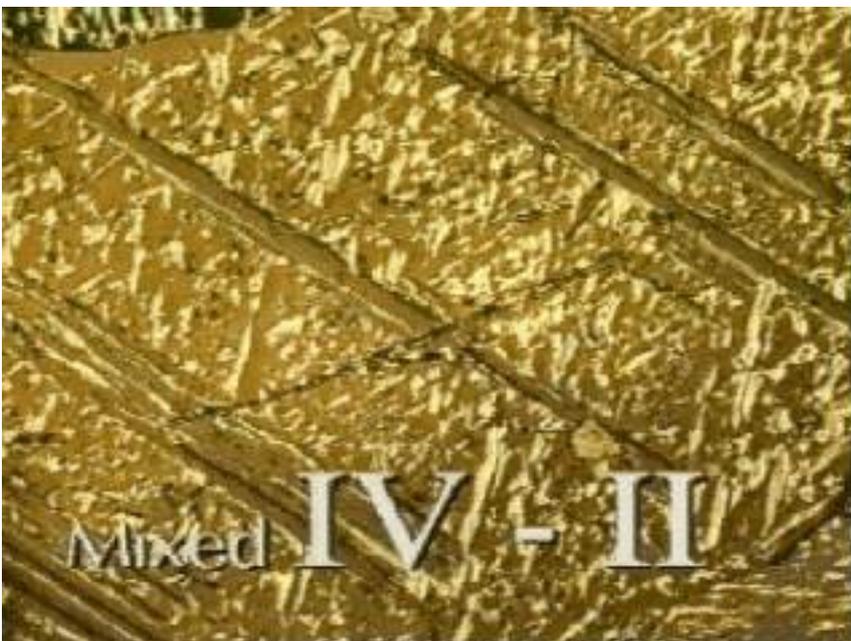
Fig. 10 Transformation of IV to II on heating through ~50°C. The banded microstructure of IV results from a process like that seen in Fig 9 and corresponds to domains of different crystallographic orientation. The movie sequence shows the bands 'fading' with heating as the complex region steadily transforms into a single orientation of phase II and this process is essentially complete by the movie's end.

Phase Transformations with an Externally Applied Stress

The II to I transformations are extremely sensitive to shear stress. The application of such a stress always induces the boundary between these phases (this boundary is initially stationary in a stable temperature gradient) to move so as to increase the volume fraction of the lower temperature phase. Under certain conditions, stress can induce spectacular instability of the phase boundary. However, the motion of the phase boundary apparently does not reflect the orientation of the applied shear stress. These types of behaviour have all been observed in thin films of NH_4NO_3 mounted between two glass slides (i.e. using techniques similar to those developed by Means 1989) on a FUTRON^{TM} in-situ deformation apparatus. The apparatus has been modified firstly by replacement of the PID heater controller by a simple Variac to produce smooth ramps when changing temperatures. Secondly, the motor drive has been disconnected to allow for constant shear stress experiments to be conducted. For such experiments (Fig. 3), the stress is applied through the action of a small mass suspended from the end of one of the glass slides via a wire that rides around a small pulley. Mass can be added or removed so that shear stress can be changed quickly and reasonably smoothly. For interpreting every image seen on this CD, note that the NH_4NO_3 film is sandwiched between two glass slides, one closer to the viewer and one further away (Fig 3). Shear stress is applied via two glass 'pistons' (e.g. east and west of static image Fig 11) so that the plane of 'pure' shear is parallel to the specimen film plane with the specimen shortening in one direction and extending perpendicular to this. The expansion of the specimen perpendicular to the film plane is not known but must be relatively minor. Care is needed interpreting the images as the shortening sense is not fixed. For all static images, shortening is oriented east-west. This is also true for most of the movie sequences but see below.
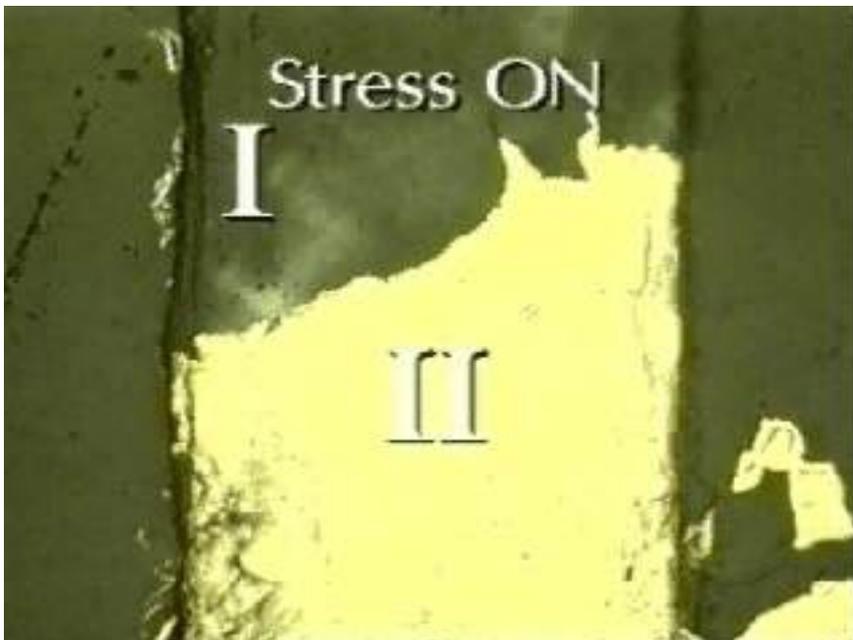
Fig. 11 The still image shows one example of transformation I to II mobilised by stress at constant 125°C. Movement of the phase boundary occurred only when the stress was applied. Several examples are shown in the movie where the glass 'pistons' loading the specimen are sometimes visible - for the first 30% of the movie the pistons advance from north and south, for the final 70% the pistons advance from east and west.

Fig. 12 This static image shows another example of transformation from I to II under stress (actually taken from the earlier movie). Stress caused the phase boundary to move northwards- phase I was consumed. The movie here shows a final example of I - II transformation under stress where the phase boundary is particularly unstable although it is not known why. No stress initially but the boundary begins to move erratically as soon as stress is applied. Shortening is E-W.

In addition to microstructural changes, permanent change of shape (ie plastic deformation) of a polycrystalline specimen might also occur during a phase transformation if a shear stress that is *less than the yield stress of the weaker phase* is simultaneously applied. Repeated cycling through a phase transformation in the presence of such an applied stress can lead to very large strains, similar to those associated with superplasticity. This effect (Meike 1993), commonly termed transformation plasticity, has been observed in many metallic systems. Recently, similar behaviour has been observed in ammonium nitrate and other ionic crystals in experiments using a simple dead-load creep apparatus with bulk specimens (McLaren and Meike, 1996). This apparent weakness of a polycrystalline ammonium nitrate specimen during a phase transformation is independent of the nature of the transformation (i.e. displacive versus reconstructive) and appears to be the result of the small external stress biasing the direction in which the relatively large internal stresses (associated with the volume change at the transformation) operate. It is these internal stresses that drive the deformation: there is no *intrinsic* weakness of the specimen during the transformation.

These observations on ionic crystals may provide important geophysical information about deformation in the neighbourhood of the major discontinuities associated with phase transition zone of the Earthís mantle (Ringwood 1991).

Fig. 13 The movie here summarises all observations using thin film NH_4NO_3., both with and without stress. 1) Microstructures change at each transformation: grainsize may increase or decrease. 2) Phase boundary has different shapes for different transformations. 3) Stress affects phase transformations. Here,

stress favours low-T phases.

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