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Twin memory and twin amnesia in anorthoclase

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ABSTRACT

Many natural minerals and synthetic materials display twin microstructures resulting from displacive phase transitions. These microstructures may be removed temporarily from the sample by heating above the relevant transition temperature, though the twinning generally returns on subsequent cooling.

In anorthoclase, the spatial distributions of twins before and after brief annealing above T_C are often identical. This property appears to be a common feature in many materials which undergo ferroelastic phase transitions, and is known as 'twin memory'. The atomic mechanisms responsible for this twin memory may be investigated by studying the annealing regimes required to remove the memory effect; how long must a sample be annealed, and at what temperature, to induce 'twin amnesia'.

High-resolution X-ray diffraction (XRD) has been used to investigate twin memory and twin amnesia in anorthoclase. In anorthoclase, the primary constraint on twin amnesia is thermodynamic, rather than kinetic. The critical temperature to induce amnesia correlates well with the top of the (Na, K) solvus in disordered alkali feldspar. For this reason, the proposed mechanism for twin memory involves the segregation of alkali cations in thin lamellae at the twin boundaries.

KEYWORDS: feldspar, twinning, X-ray diffraction, twin memory, ferroelastic, phase transition.

Introduction

TWIN microstructures in minerals may result from a number of mechanisms, such as orientational stacking errors during crystal growth, macroscopic deformations in response to an external stress, and the microscopic strains resulting from structural phase transitions. In all of these cases, the local structure of the twin will differ from that in the bulk (Hayward *et al.*, 1998; Salje *et al.*, 2000). These changes affect a wide range of crystal properties, such as bulk elastic constants and transport properties, and so are relevant in both a geological context and for the use of minerals and related crystalline materials in technological applications.

Transformation twins may be distinguished from growth and deformation twins by the fact that transformation twinning is lost when a twinned sample is heated above the critical temperature for the transformation. Cooling back below T_C will cause the twinning to return. In a number of systems, the twins have been found to have the property where the microstructures seen before and after such a heating cycle are identical, a phenomenon known as twin memory. This effect has been studied in a number of systems, including quartz (Frondel, 1945; Heaney and Veblen, 1991; Xu and Heaney, 1997), anorthite (Xu and Heaney, 1997), the YBCO superconductor (Voronkova and Wolf 1993), and a number of incommensurate phases reviewed by Strukov (1989).

In this article, we describe the results of a study of the processes of twin memory and memory loss in the disordered alkali feldspar anorthoclase. In addition to its intrinsic interest, measurements of twin memory and twin amnesia can be used to gain insights into the ways in which mineral transformation processes interact with each other and with crystalline defects.

Principles of twin memory

The first detailed study of twin memory processes in minerals was a study of quartz, by Frondel

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(1945). In this case, the main interest was technological – quartz was being used as a radio frequency standard, an application which requires reasonably large untwinned crystals. Twin memory created a difficulty in this case, since it was impossible to detwin quartz crystals by simply heating them above the α-β phase transition. Frondel studied the effects of prolonged annealing above the transformation temperature, and proposed that some mechanism was inducing strain fields within the crystals independently of the twin structure. Twin memory was thus a result of the interaction between these strain fields and the spontaneous strain associated with the α-β phase transition.

These ideas were further developed by Heaney and Veblen (1991). Their model of twin memory starts by considering a twinned phase (Fig. 1*a*). Any real solid will contain defects of various kinds, such as vacancies on various atomic sites, impurity atoms and dislocations. It is likely that some species of defect will be thermodynamically more stable on the twin boundaries, rather than in the bulk material. Over long periods of time, it will be possible for these defects to collect on the twin walls, as shown in Fig. 1*b*. If this sample is then heated above the transformation temperature, the twins and twin boundaries will vanish, but the positions of the former domains will still be marked by the collection of defects where the boundaries previously were, as in Fig. 1*c*. On cooling, the local strain around these defect-rich planes will cause the twin boundaries to re-form on their original sites. As a result, the twin microstructures observed before and after heating above T_C for a relatively short time would be the same.

If the sample temperature remains above T_C for long enough, the defects will eventually disperse. Once this has happened, there will no longer be any reason for the twin boundaries to form in specific locations, and the memory effect will be lost. This factor is important, since it provides a means by which the atomistic mechanisms responsible for twin memory may be studied. If the time and temperature dependencies of twin memory loss (or twin amnesia) are known, it may be possible to determine what species of defects are principally responsible for the memory effect in a given material.

Experimental method

Microstructural effects such as twin memory are usually most conveniently studied using various types of microscopy – optical microscopy and transmission electron microscopy being the most obvious and widely used examples. Optical microscopy is constrained by its finite resolution, so that fine-scale features cannot be observed. Transmission electron microscopy offers much better resolution, but also has significant disadvantages. One potential problem is that the area of a typical TEM image is quite small – statistical questions (such as how well a twin microstructure is preserved during a heating cycle) are hard to answer with a high precision. Provided the difference between a microstructure resulting from twin memory, and one associated with twin amnesia, is clear enough, this problem is not too serious.

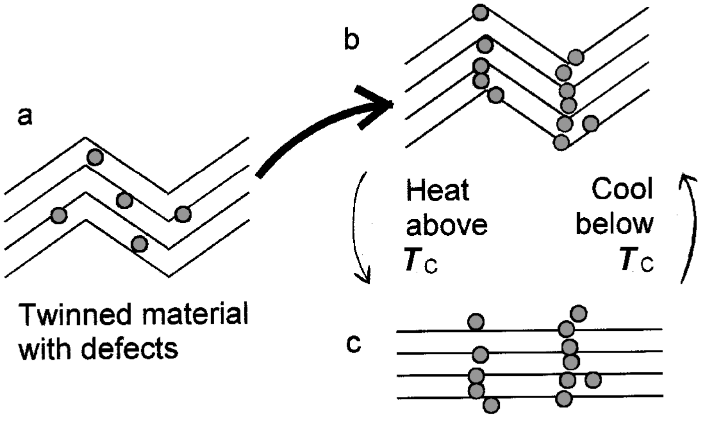

FIG. 1. Schematic illustration of atomic-scale mechanism of twin memory.

A more fundamental problem is that transmission electron microscopy is a relatively invasive technique for the study of solids; the sample is first thinned under an ion beam, and then irradiated by a beam of high-energy electrons. Not all minerals are stable under these conditions – frameworks stuffed with alkali cations are particularly prone to damage. In addition, the thinness of TEM foils can create additional stresses within a sample. These may also interact with the twin structures, leading to additional memory effects. Xu and Heaney (1997) noted this behaviour in quartz.

An important development in recent years has been the use of XRD experiments to study crystal microstructures, reviewed by Locherer *et al.* (1996). Although it is not possible to generate complete real space microstructural images from an XRD image, it is possible to describe the microstructure statistically, based on factors such as the shape and orientation of the diffraction signal.

In these experiments, a two-circle diffractometer (X1 in Locherer *et al.* 1996) was used in conjunction with a platinum-rhodium stage capable of heating the sample *in situ* from room temperature to well beyond the melting point of feldspar. The sample was attached to this stage with silver paste to ensure good thermal contact.

Sample characteristics

The sample studied was an anorthoclase with composition $Ab_{70}Or_{25}An_5$ from volcanic tuffs in Camperdown, Victoria (Sample 195127 in the Harker Collection, Cambridge University). (001) cleavage slices were mounted on the sample stage with the rocking axis ω parallel to [100]. 002 was a convenient strong reflection for study. A single peak is seen in a plot of $I(2\theta)$ at $2\theta = 27.9°$. This peak remained a sharp single peak throughout the experiment, implying that no macroscopic exsolution took place. The room temperature $I(\omega)$ rocking curve (lowest curve in Fig. 2) shows three peaks; the peaks at $\omega = 11.5°$ and $16°$ correspond to the two orientations of albite-twinned domains, whereas the central peak is the diffraction signal from the parts of the crystal twinned according to the pericline twin law.

All three peaks, but particularly the peak at $\omega = 16°$, are relatively broad and rough. This is related to the fact that the twin microstructure is comparatively heterogeneous, with a number of needle domains, local strain fields and suchlike.

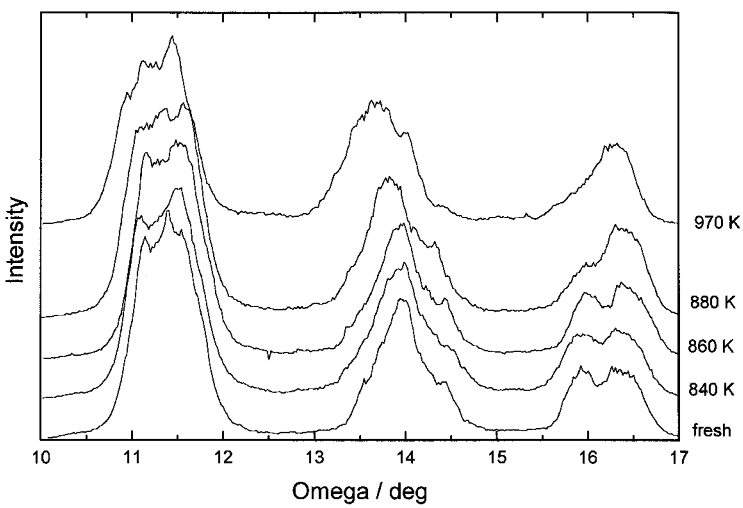

FIG. 2. Rocking curves for the 002 reflection in anorthoclase as a function of annealing temperature. The lowest curve shows the rocking curve obtained from a fresh crystal. This sample was subjected to annealing cycles of 4 h duration at progressively higher and higher temperatures. The diffraction signals obtained after anneals at 840 K and 860 K are quite similar, indicating that the 860 K annealing run did not induce significant twin amnesia. However, significant changes are seen after the 880 K run. The overall effect of annealing is to cause the rocking peaks to become smoother (as shown by the rocking curve seen after the 970 K anneal).

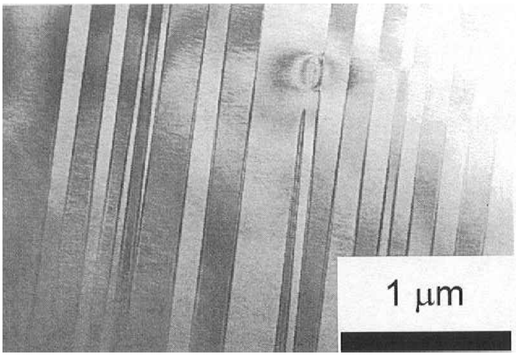

FIG. 3. Typical TEM micrograph of anorthoclase. This image is of a (010) slice of Camperdown anorthoclase, and shows the pericline twins approximately parallel to (001).

Figure 3 shows a typical TEM image of this sample (albeit of pericline, rather than albite twins), and illustrates the heterogeneity of the microstructure.

Heating regimes

The overall aim of an experiment involving twin memory and twin amnesia is to determine the annealing conditions required to cause twin memory to be lost. The experimental strategy is to record the twin microstructure at room temperature, anneal the sample under a certain set of conditions, cool back to room temperature, and compare the microstructure seen after annealing with that seen before. By repeating this process for a range of different sets of annealing conditions, we obtain the data required for the thermodynamic/kinetic analysis of the mechanism causing twin memory.

After collecting the room temperature rocking curve of anorthoclase, the sample was heated rapidly in a vacuum to some high temperature above the displacive transition temperature for the sample (733 K); this temperature was maintained for 4 h. The sample was then cooled back to room temperature (with a cooling rate of ~10 K min^{-1}), where the rocking curve was again recorded. The cycle of collecting a room temperature rocking curve and heating to progressively higher and higher temperatures was repeated until an annealing temperature of ~1000 K was reached. The positions of the rocking maxima at room temperature were not affected by heating, which provides some confirmation that the sample did not move during the experiment.

Results

Rocking curves as a function of annealing temperature

The stack of rocking curves in Fig. 2 shows the effect on the rocking curves of 4 h annealing at the stated temperatures. Annealing at 860 K does not induce much, if any, twin amnesia. There are some changes in the profile of the $\omega = 11.5^\circ$ peak, and a slight shift in the $\omega = 16^\circ$ peak, but the central peak is reproduced almost perfectly. However, these changes are relatively slight, and it seems reasonable to describe this pair of rocking curves as an example of twin memory.

Annealing at 880 K has a rather greater effect. The most important change is the loss of one of the two peaks in the pair at $\omega = 16^\circ$. A similar loss of fine structure can be seen, though on a less dramatic scale, in the other two peaks as well. This smoothing of the rocking curves can be seen more clearly by examining the rocking curve seen after annealing at 970 K (top curve in Fig. 2).

In real space, the loss of roughness in the diffraction peaks implies that the microstructure is becoming more uniform; in other words that the bent, or misaligned twins are the ones that are being annealed out preferentially during the heating. This is consistent with the fact that it is the misaligned twins that have the highest excess free energy; the energy cost of a single twin in an ideal orientation is quite small (see, for example, the calculation in Hayward *et al.* 1998).

Discussion: a possible mechanism of twin memory in anorthoclase

Natural feldspars display a number of interacting solid-state transformation effects, which could lead to local defects causing the pinning of twin boundaries and twin memory associated with the displacive phase transition. To determine the main mechanism associated with the twin memory, we must consider how the thermodynamics and kinetics of memory loss correlate with those of the candidate processes.

Although the data currently available do not answer this question conclusively, many mechanisms can be excluded. For example, one possibility would be that the excess CaAl in this anorthoclase is pinning the twin walls. However, the diffusion of Al through the feldspar structure at 880 K is so slow that negligible twin amnesia would be expected at this temperature (Yund and Tullis, 1980).

The diffusion of most other defects (such as other alkali cation species, or excess oxygen) through the feldspar structure should be sufficiently rapid to cause significant memory loss after the annealing cycles used here (e.g. Yund *et al.*, 1989). However, then it is not obvious why twin memory is preserved until the 880 K anneal.

Consideration of the phase diagram for anorthoclase (Fig. 4) highlights one likely mechanism. The temperature at which twin memory begins to be lost is near the solvus temperature for anorthoclase with the composition of the Camperdown sample. For this reason, segregation between Na and K is a plausible mechanism for the twin memory effect.

The local crystal structure of the twin boundary will differ from that in the bulk (Hayward *et al.*, 1998; Bismayer *et al.*, 2000; Salje *et al.*, 2000), and this is likely to have the effect of making the alkali sites within the twin boundary (typically a layer several unit cells thick) a preferred site for either Na or K. Simple symmetry and volume arguments would seem to favour the larger K ions on the twin boundaries, and Na in the bulk, but this has not been confirmed in detail.

If alkali segregation is the mechanism responsible for twin memory in anorthoclase, we would expect memory loss to occur quite rapidly once the solvus temperature is exceeded, since alkali diffusion through the feldspar structure is rapid (Yund *et al.*, 1989), and the diffusion lengths required for twin memory are quite small.

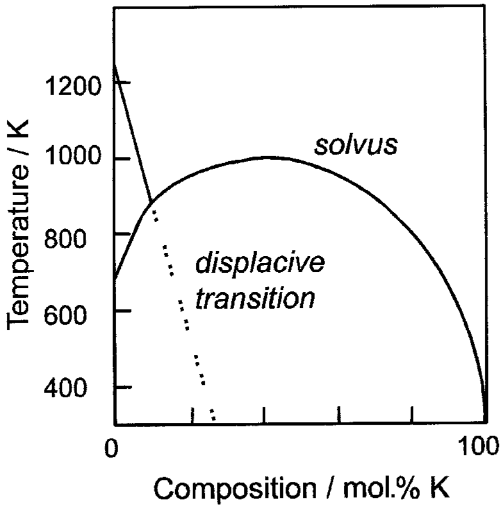

FIG. 4. Schematic phase diagram for anorthoclase, after Smith and Brown (1988).

At room temperature, the twin wall thickness in anorthoclase is of the order of 25 Å (Hayward *et al.*, 1996; this measurement is for the pericline wall, but the thickness of the albite wall is likely to be similar). The bulk composition of the sample is around $Ab_{70}Or_{25}An_5$. There are thus sufficient K cations to completely fill the twin wall in a relatively narrow layer. In principle, the maximum diffusion length required is of the order of 1–2 wall thicknesses.

If this model is correct, the kinetic control of twin memory and twin amnesia in anorthoclase is likely to be far less important than the thermodynamic control. Below the solvus temperature, cation segregation is stable and so little or no memory loss should be seen, even for prolonged annealing. Above the solvus temperature, cation diffusion is rapid enough that twin amnesia should occur almost immediately. Further experiments to investigate the time axis of the TTT graph in more detail are needed to fully constrain the memory properties of anorthoclase.

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