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Observation and kinetic analysis of a memory effect at the α-β quartz transition

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ABSTRACT

Positions and orientations of the Dauphiné twins in α quartz were monitored as specimens were cycled about the α-β transition temperature in a transmission electron microscope, and a remarkably faithful memory effect was observed. In a set of kinetic experiments, changes in the Dauphiné twin positions were analyzed as a function of time and temperature above T_i, the transition temperature between the incommensurate phase and β quartz. When specimens were annealed slightly above the transition temperature for varying periods, the degree of memory loss displayed "λ-type" behavior: memory loss increased to a certain point and then dropped precipitously to a constant value. On the other hand, when the temperature of overheating was increased and annealing time was held constant, the memory loss increased.

The mechanism responsible for the observed hysteresis is not known with certainty, but possible causes include strain effects, the persistence of twin domains above the transition point, and pinning of domain walls by point defects. Because our observations show that memory loss is a thermally activated process, pinning by point defects is the most likely explanation for the memory effect.

INTRODUCTION

When the United States entered World War II in 1941, it was confronted with the need to produce tens of millions of quartz oscillator plates for radio communications. With the science of crystal synthesis still in its infancy, the procurement of an adequate supply of high-quality natural quartz crystals appeared as a problem of the greatest urgency. The War Department responded to this crisis by organizing civilian and military materials scientists into a Quartz Crystal Coordination Section. The initiation of this enterprise is described by Frondel (1945a), and the fruits of its 4-yr investigation into the properties of quartz constitute an entire issue of the *American Mineralogist* (May–June, 1945).

Because this country could boast of only a few deposits of high-grade quartz crystals, the Coordination Section tried to develop methods to eliminate the imperfections in defective specimens. One of the most common of these defects is the Dauphiné twin, which is produced during the inversion from β to α quartz. Because the **a** axes of adjacent Dauphiné twins are rotated 180° relative to each other, the piezoelectric charges induced in one set of twins by compression normal to **c** will cancel the charges created in the other. To be useful as oscillators, such crystals must be "detwinned"—that is, converted entirely to one of the two Dauphiné orientations.

Frondel (1945b) attempted to remove the twins present in natural quartz samples by heating specimens above the α-β transition temperature and then cooling them slowly. To his surprise, fewer than 10% of the crystals thus treated could be detwinned successfully; even samples annealed at 1000 °C remained twinned when reexamined at room temperature. On the other hand, this method proved quite effective for removing twins that had been induced artificially in crystals that originally were perfect. Thus, it would appear that the quartz plates somehow remembered their initial twin state even after transforming to their high-temperature form.

This ability of quartz to retain twin information after cycling about the transition temperature is not immediately explicable from a purely crystallographic view of twin formation. When the β polymorph is cooled below the transition temperature of 573 °C to α quartz, the tetrahedral chains kink in one of two possible directions, thereby reducing the rotational symmetry along the screw axes from sixfold to threefold; the space group of the α phase ($P3_221$ or $P3_121$, depending on chirality) is a subgroup of that of the higher-temperature β phase ($P6_222$ or $P6_422$). The two possible directions of tetrahedral rotation give rise to the two Dauphiné twin orientations, which are related by the twofold rotation lost during the transformation.

When α quartz transforms to β quartz, the twofold symmetry along **c** is restored, and the twins should disappear, since they are related by a 180° rotation. Consequently, there is no obvious basis for the retention of twin information after a specimen has been heated above the transition point. The observation by dark-field transmission electron microscopy (TEM) of an intermediate phase between the stability fields of α and β quartz by Van

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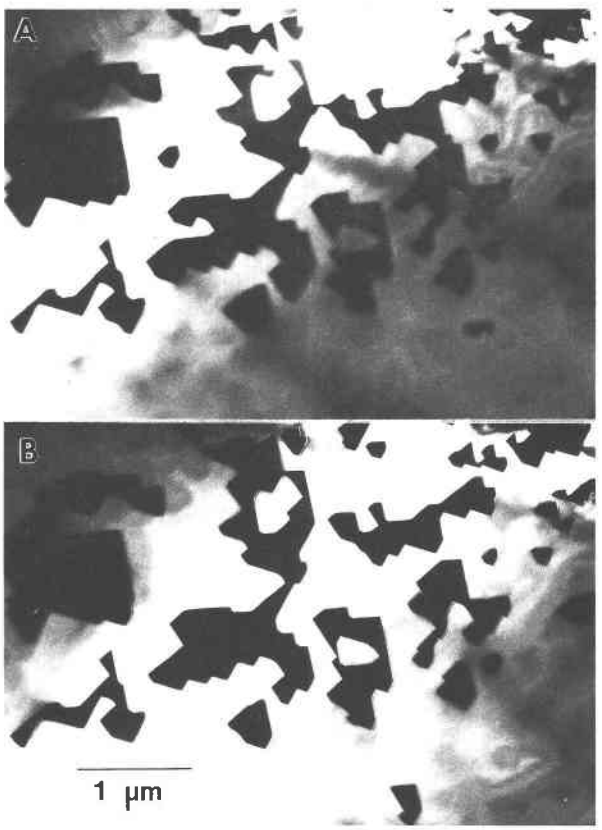

Fig. 1. Dark-field (**g** = 301) images of Dauphiné twin domains. (**A**) Original twin configuration. (**B**) New twin configuration after the specimen has been heated above and then cooled below T_i. Although some differences can be discerned, the similarity is striking.

Tendeloo et al. (1976) only added to the confusion; this incommensurate structure forms by the dispersal of preexisting Dauphiné twin domains into an ordered array of Dauphiné microtwins, which grow finer over a 1.3 °C temperature interval until the structure enters the β stability field (see review by Heaney and Veblen, 1991). It therefore is certain that the macroscopic twins do vanish at the transition point.

Nevertheless, experiments following those of Frondel substantiate his interpretation of a memory effect in quartz. Single-crystal X-ray diffraction experiments of a rose quartz specimen cycled about the transition temperature showed that after each cooling episode the volumes occupied by the two Dauphiné twin orientations remained remarkably constant (Young, 1962). Although the twin volumes in other quartz samples varied unpredictably, the ratio of the volume of one twin orientation to the other typically settled into a constant value after ~20 cycles. In addition, Inoue et al. (1974) and Zarka (1983) observed with X-ray topography a close correspondence in the positions of Dauphiné twin boundaries before and after heat treatment. Similarly, the reappearance of twin domains close to their initial configurations as discerned from electron micrographs is noted by Malov and Sonyushkin (1976) and Dolino and Bachheimer (1982).

In the course of our TEM experiments on the incommensurate and β phases of quartz (Heaney and Veblen, 1991), we also noted the fidelity with which the Dauphiné twin boundaries returned to their original locations and orientations (Fig. 1). However, some movement of the twin boundaries after a series of temperature cycles did occur (Fig. 2), and in an effort to characterize this memory effect, we performed two sets of kinetic experiments: (1) Specimens were heated to successively higher temperatures and held at those maximum temperatures for a constant period before quenching. (2) Specimens were annealed at a constant temperature for varying periods. The Dauphiné twin configurations before and after each cycle were compared and the degree of memory loss computed. The results of these experiments are described below.

Experimental procedures

Experiments were performed on samples cut from a transparent, doubly terminated quartz crystal from Hot Springs, Arkansas (U.S. National Museum no. R17684-2). Thin sections were cut normal to the morphological c axis and thinned further by Ar ion milling. Unsupported foils of 3-mm diameter were then coated lightly with amorphous C.

Electron microscopy was performed with a Philips 420 microscope equipped with T or ST objective lenses and operated at 120 keV. Heating experiments were carried out with a Gatan model 628 single-tilt heating holder. Specimens were heated by an annular Ta furnace, which warmed in response to increases in electrical current through a Mo strip heater. Furnace temperatures were registered by a Pt-13% Rh thermocouple spot welded to the furnace body. The furnace was heated to the quartz transition temperature at a rate of about 5 °C per min and allowed to stabilize for 1 h before experiments were begun. X-ray analyses in the TEM were obtained with an EDAX energy-dispersive spectrometer (EDS) and a Princeton Gamma-Tech System IV analyzer, and no elements other than Si were observed.

The transition temperature between α quartz and the intermediate phase is denoted as T_c, whereas the temperature at which the intermediate phase transforms to β quartz is called T_i. Previous studies (e.g., Bachheimer, 1980; Dolino et al., 1984) indicate that T_i is approximately 1.3 °C above T_c, where T_c = 573 °C. Over the course of this investigation, specimens were heated above T_i to a maximum annealing temperature (T_{max}) and held at that temperature for a specified period. We here define the difference between the critical temperature T_i and the maximum temperature T_{max} as the temperature of overheating ΔT_o ($\equiv T_{max} - T_i$). The furnace temperature corresponding to T_i of the specimen was inferred from the disappearance of the intermediate phase in dark-field (**g**

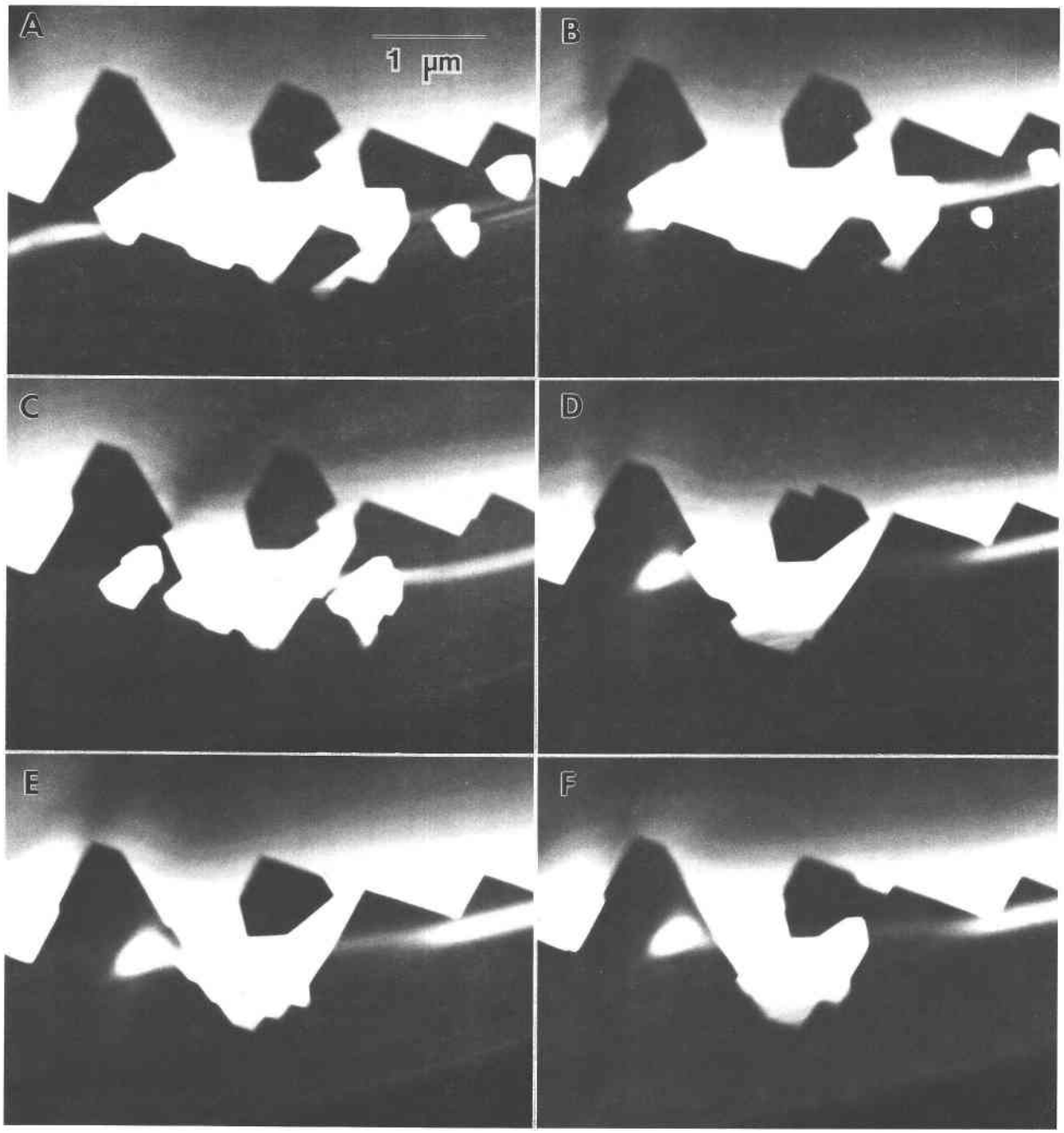

Fig. 2. A series of dark-field (**g** = 301) images after the specimen has been cycled repeatedly about the transition temperature. Correspondence is close from cycle to cycle, but original and final twin configurations are distinctly different. From experiment 2 with ΔT_o = 3–5°. (**A**) Annealing time t at T_{max} = 14 s; (**B**) t = 45 s; (**C**) t = 66 s; (**D**) t = 130 s; (**E**) t = 195 s; (**F**) t = 300 s.

= 301) images. After annealing at T_{max}, specimens were quenched to approximately 5° below T_c, and dark-field images of the twin domains were recorded with **g** = 301.

Four separate experiments were conducted under the following conditions: (1) annealing time at T_{max} was increased from one cycle to the next from 1 to 300 s and ΔT_o was held constant at 1–2°; (2) annealing time from cycle to cycle was increased from 1 to 1800 s and ΔT_o was held at 3–5°; (3) ΔT_o was increased in successive cycles from 16 to 255° and annealing time at T_{max} was held constant at 15 s; and (4) ΔT_o was varied with each cycle from 14 to 207° and annealing time at T_{max} was 90

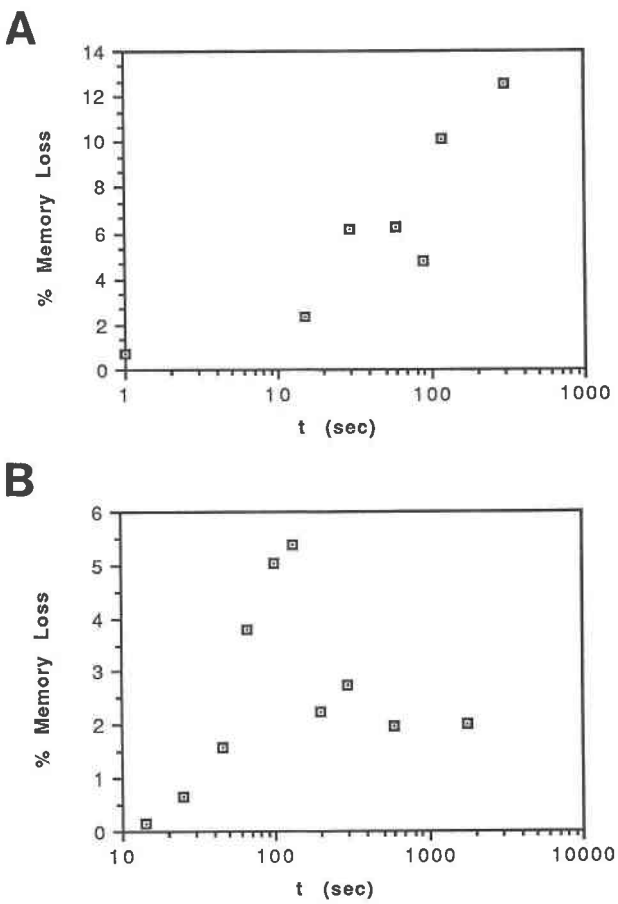

Fig. 3. Plots of memory loss with time such that temperatures of overheating were held constant. Data points represent memory loss per cycle. (**A**) Plot of percentage memory loss vs. annealing time at T_{max} with ΔT_o = 1–2° (experiment 1). (**B**) Plot of percentage memory loss vs. annealing time at T_{max} with ΔT_o = 3–5° (experiment 2).

s. It should be noted that performance of these experiments was hindered by the friability of the specimens, thereby limiting the amount of data obtained.

Memory loss was measured by overlaying the projected image of a given twin configuration onto the traced image of the previous configuration. Images were rotated and translated to achieve the best fit as determined by eye. Regions in which Dauphiné twin orientation had changed during the heating cycle were then traced, and the areas within those regions were measured with a Numonics Model 2400 DigiTablet graphics analysis system. The percentage of memory loss was computed by dividing the sum of the areas with changed orientation by the total area examined, which varied from 4 to 32 μm^2.

Results

The results of the experiments are plotted in Figures 3 and 4. It should be emphasized that the data points represent memory loss per cycle, not cumulative memory loss.

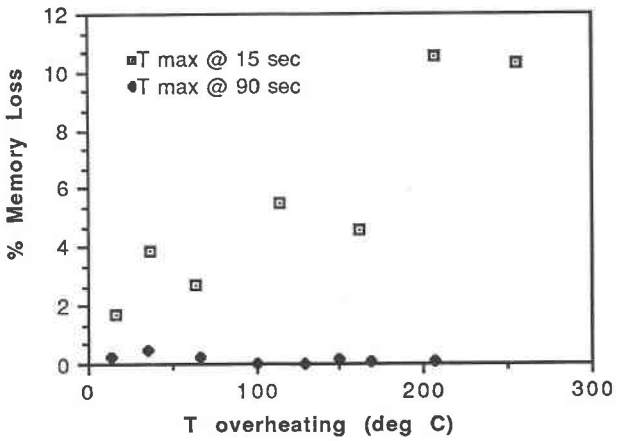

Fig. 4. Plots of percentage memory loss vs. temperature of overheating such that annealing times were held constant. Data points represent memory loss per cycle. Open squares represent experiment 3 with annealing time at T_{max} = 15 s. Filled dots represent experiment 4 with annealing time at T_{max} = 90 s. Note that the sample used in experiment 4 had been cycled previously and cooled to room temperature for 4 weeks.

When a specimen was cycled a total of seven times about T_i with ΔT_o = 1–2° and annealing times ranging from 1 to 300 s (experiment 1), the degree of memory loss typically increased after each cycle (Fig. 3A). However, a different behavior was observed when a specimen was cycled ten times about T_i with ΔT_o = 3–5° and annealing times increased from 1 to 1800 s (experiment 2). In this experiment, the increase in memory loss peaked after the sixth cycle at an annealing time of 130 s and decreased to a smaller and relatively constant amount of change thereafter. The resulting graph of percent memory loss vs. ln t assumes a λ shape (Fig. 3B).

The foil heated to increasing T_{max} for 15 s in experiment 3 showed an overall increase in memory loss with higher ΔT_o (Fig. 4). When these results are expressed as an Arrhenius function such that the natural log of the percentage memory loss is plotted against the reciprocal of T_{max}, a linear relationship can be discerned, with a correlation of −0.89 (Fig. 5).

The specimen annealed for 90 s at T_{max} in experiment 4 displayed only minor discrepancies in boundary positions after the first few cycles and thereafter remained virtually unchanged (Fig. 4) Even when heated over 200° above T_i, virtually no boundary movement was easily discernible. However, it is important to note that the sample used in experiment 4 had been cycled previously during experiment 2. It had cooled to room temperature and been stored for 4 weeks before it was reused for experiment 4.

Interpretation

The mechanism that governs the memory effect in quartz is not well understood, but three possibilities may be proposed: (1) constraints on the twin-wall positions by strain fields in the quartz foils, (2) persistence of the Dau-

phiné twins above the transition temperature, and (3) pinning of the twin boundaries by point defects. We shall discuss these possibilities in turn.

Effects of strain fields

That Dauphiné twins are intimately related to structural strain has been known for over half a century. Schubnikow and Zinserling (1932) demonstrated that at room temperature quartz will twin under an applied stress, and Frondel (1945b) observed that Dauphiné twinning could be induced by quenching a specimen heated to temperatures well below T_c, presumably in response to the strain gradients generated by the sudden heat loss. Further, Frondel noted that in specimens cycled about the transition, the degree of twinning stood in inverse proportion to the concentration of cracks; Dauphiné twins seemed to absorb internal strain. Lastly, it is clear not only from Frondel's work but from the X-ray topographic experiments of Zarka (1983) and our own TEM studies that Dauphiné twin shapes follow the outlines of cracks and subgrain boundaries in quartz crystals.

Since these twins obviously are quite sensitive to ambient strain fields within the specimens, it is possible that the memory effect observed during our experiments was merely an artifact of the surface strain inherent in the extremely thin foils required for transmission electron microscopy. Although this interpretation cannot be ruled out entirely, some factors suggest that the role played by structural strain was a minor one. Despite the similarity in twin configurations from one cycle to the next, changes did occur, and the difference between the initial and final configuration after a series of heat treatments could be marked indeed. In addition, memory behavior has been observed in bulk samples of quartz: Frondel (1945b) examined square plates measuring 19 mm on an edge and 0.38 mm thick; Young (1962) performed X-ray diffraction on single crystals of quartz; and Zarka (1983) analyzed plates with dimensions of 10 × 10 × 1 mm.

Unlike large twin domains, small twins at the very edges of the thin foils displayed no alteration after repeated cycling, and they did not coarsen in the usual fashion upon cooling to room temperature. We concluded that these twins were pinned by extreme surface strain or by strain resulting from bending of the crystal at the thinnest part of the foil. Such very thin areas were not used in our experiments.

Persistence of Dauphiné twins in β quartz

That twin character persists above T_c may be suggested by the propensity of the triangular microtwins that comprise the intermediate phase to assemble into ordered arrays known as "macrodomains" (Van Tendeloo et al., 1976; Van Landuyt et al., 1985). These macrodomains occur in two orientations, and Snoeck et al. (1986) observed one of these macrodomains alternately disappear and reappear within a larger macrodomain matrix. In addition, Yamamoto et al. (1988) propose that at the critical temperature the angle separating the oriented

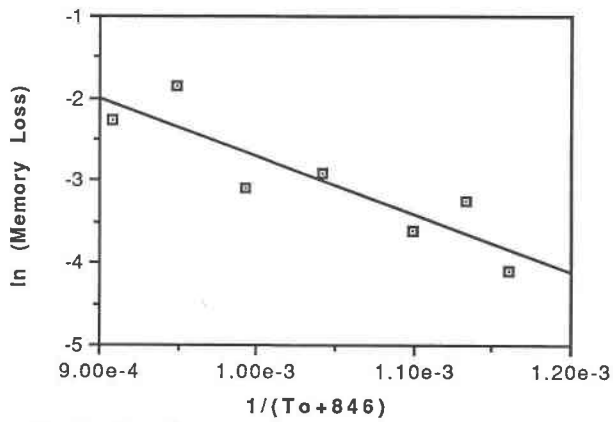

Fig. 5. Data from experiment 3 plotted as an Arrhenius relationship. Correlation is −0.89.

macrodomains is identical to the angle between the Dauphiné twin walls in α quartz. This equivalence might suggest a structural continuity between the Dauphiné twin domains of α quartz and the macrodomains of the intermediate phase. However, when we compared the positions of many sets of macrodomains within the intermediate phase with the locations of the Dauphiné twins formed after quenching the crystal below T_c, we discerned no correspondence whatsoever.

Another possible explanation for the memory effect is that Dauphiné twins may not truly vanish at T_i but rather may continue to exist through the incommensurate phase and into β quartz. Such behavior would be similar to that observed at the low–high leucite phase transition at ~655 °C. This transformation involves an inversion from what was thought to be an untwinned cubic structure to a twinned tetragonal one (Peacor, 1968; Sadanaga and Ozawa, 1968). However, TEM analysis of the transition (Heaney and Veblen, 1990) indicated that the high-temperature structure was not rigorously cubic; thus, the leucite "memory effect" occurs because the twins never are destroyed.

The memory effect in quartz, however, clearly differs from that in leucite. When leucite is heated above the critical temperature, the twin walls remain stationary and grow steadily fainter. By contrast, the Dauphiné twin walls of quartz vibrate violently just below T_c, and at the critical temperature the large twin domains can be seen to disperse into the mosaic of microtwins that constitutes the intermediate phase of quartz. Thus, it seems certain that the Dauphiné twins in quartz truly are destroyed at the transition.

Boundary pinning by point defects

Memory effects caused by point defects are conspicuously common in materials with incommensurate structures (see Strukov, 1989, for review), such as deuterated thiourea (Jamet and Lederer, 1983), barium sodium niobate (Errandonea et al., 1984; Manolikas et al., 1987), and Rb_2ZnCl_4 (Unruh, 1983). Typically, the hysteresis is

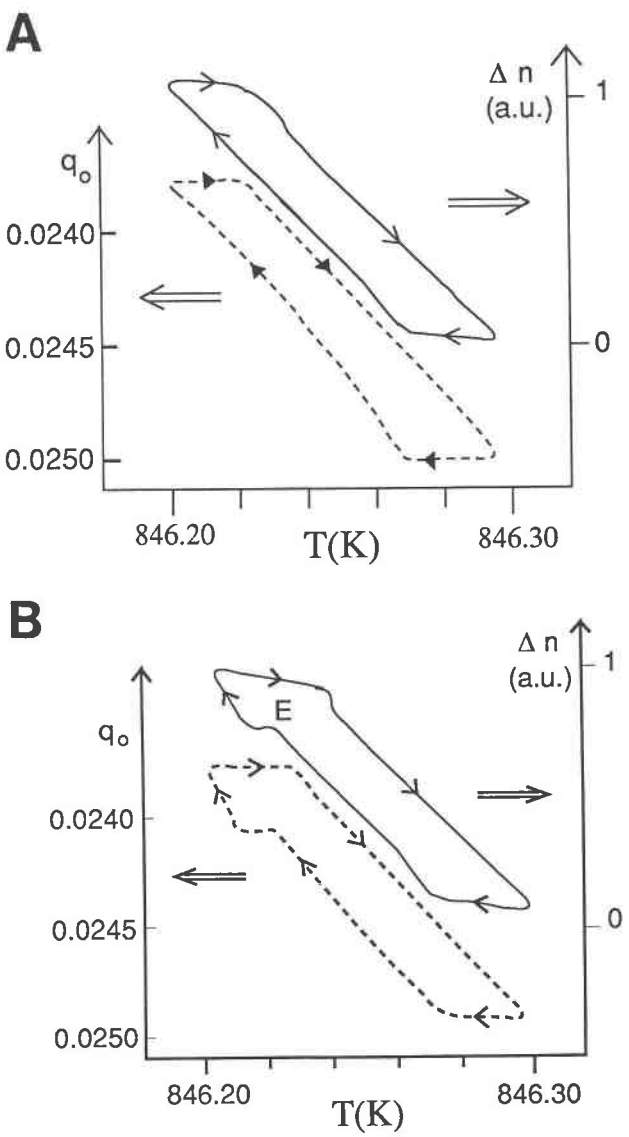

Fig. 6. Graphs of the variations of the modulation wavevector $\mathbf{q}_0$ of the intermediate phase (dashed curve) and of the birefringence Δn (full curve) with temperature. (**A**) A 16-h cycle about T_i reveals a global hysteresis in $\mathbf{q}_0$ and in Δn. (**B**) Same conditions as in A except that the specimen was held at temperature E for 12 h before the cycle. The kink in the curve at E is evidence of a memory effect. (After Dolino, 1985.)

manifested when the modulated substance is annealed at a specific temperature T^* within its incommensurate stability field and then cycled through that annealing temperature from above and below; when the material approaches T^*, it displays an anomaly in such properties as electrical susceptibility, optical birefringence, or resistivity (Jamet, 1988).

If the material is heated well above T^* for a sufficiently long time, this hysteresis can be erased. Lederer et al. (1984) explained these memory phenomena as resulting from an organization of point defects. They theorized that point defects acquire their own periodicity if they are allowed to interact with a modulated structure for an extended period, thereby creating so-called defect density waves. These defect modulations are metastable, and they can affect the macroscopic properties of the material.

These results are germane to this study because exactly this kind of memory effect has been observed in the incommensurate phase of quartz (Dolino et al., 1988). If a crystal of quartz is held at a specific temperature within the stability field of its intermediate phase for 10–20 h, the structure will "stall" during subsequent heating-cooling cycles when that temperature is reached; graphs of the modulation vector $\mathbf{q}_0$ (Bastie and Dolino, 1985) and of birefringence (Dolino, 1985) against temperature are kinked at the annealing point (Fig. 6). Bastie and Dolino also observed a "small but clear emission of heat" when specimens reached these temperatures, and they attributed the hysteresis to mobile defects.

Point defects in the form of vacancies, impurity substitutions, and interstitials are common in natural quartz crystals. Substitutional Al atoms adjoining O atoms with an electron deficiency give rise to smoky quartz (O'Brien, 1955), and interstitial Fe is believed to cause both the color and the Brazil twinning characteristic of amethyst (Cohen, 1985). The conductivity of quartz because of diffusion of interstitial Li^+, Na^+, and K^+ cations along the channels parallel to the **c** axis of quartz has been investigated by a number of scientists (see Freer, 1981, for review). In addition, the incorporation of H in quartz as molecular H_2O and as OH using the exchange $Si^{4+} \leftrightarrow 4H^+$ has been studied extensively (Griggs and Blacic, 1965; Paterson and Kekulawala, 1979; Aines et al., 1984; Cordier et al., 1988).

Clearly, even within the nearly perfect natural quartz crystals used in these experiments, point defects are abundant and diverse, and indirect evidence from previous studies suggests that the memory effects we observed resulted from the immobilization of the twin boundaries by defects. For instance, it has been suggested that the structure of α quartz locally changes to the ideal β configuration at the Dauphiné twin walls (Liebau and Böhm, 1982), and it seems likely that the environment of these boundary regions might be energetically favorable for certain defects. In fact, Young (1962) reports that in some samples of quartz, the ratio R of one Dauphiné twin orientation to the other would "flip" after a heating cycle to $1/R$. This inversion suggests that the memory of the Dauphiné twins resides not within the domains themselves but along their borders. Young (1962) also observed that initial twin volumes were retained best in samples of rose quartz that contain trace amounts of Ti^{3+} (Cohen and Makar, 1985). Lastly, it should be noted that memory effects observed among antiphase domains in anorthite (Müller and Wenk, 1973) have been attributed to defects and impurity cations situated on the antiphase boundaries (Ghose et al., 1988).

Boundary wall migration and point defect diffusion

If point defects indeed pin the Dauphiné twin boundaries, then the memory loss because of migration of those boundaries may result from the diffusion of the defects. Furthermore, if the memory loss is assumed to be a linear function of time, then the change in memory loss with time may be equal to a rate constant that is directly related to the diffusion coefficient. The diffusion rate D typically follows the Arrhenius relation and can be expressed in the form $D = D_0 e^{-Q/RT}$, where D_0 is constant, Q is the activation energy, R is the universal gas constant, and T is temperature (see Manning, 1968, for review).

Therefore, the percent memory loss can be plotted as an Arrhenius function when annealing time at T_{max} is held constant and temperature of overheating is varied, and such plots should be linear, as is observed in Figure 5. This result supports the idea that point defects pin the boundaries, and it raises the possibility that the movement of the Dauphiné walls can yield values for diffusion coefficients of point defects in quartz at the relatively low temperatures attending these experiments. However, the assumption that percent memory loss is a linear function of time appears not to hold after repeated cycling of the specimens about the transition temperature, as evidenced by the precipitous drop in memory loss after the seventh cycle in experiment 2 (Fig. 3B).

Nevertheless, the λ-type behavior of experiment 2 itself may be explained on the basis of point defect diffusion. If a defect encounters a dislocation or subgrain boundary in the course of its migration, energetic considerations may discourage further diffusion, and subsequent movement of the domain wall might require migration of the entire dislocation array. Alternatively, an interstitial impurity cation might cease to migrate upon reaching a vacant site. Under such circumstances, memory loss would be expected to decrease to a low value.

In addition, diffusion of defects to energetically favorable environments may explain the observation of Young (1962) that the ratio of one twin volume to the other stabilizes after repeated cycling. Likewise, defect pinning may account for the virtually perfect memory displayed during experiment 4 (Fig. 4), since this sample had been cycled previously and cooled to room temperature for 4 weeks before it was reused. Heating this specimen more than 200° above T_i produced no deterioration in memory, suggesting that in some cases extremely high activation energies must be overcome to remobilize the defects.

Conclusion

It is clear from our experiments that quartz manifests a memory effect with regard to the position of its Dauphiné twin boundaries and that the fidelity of that memory can be remarkably strong. Further, we have demonstrated that the memory loss in quartz is a function of the maximum temperature to which a crystal is heated above T_i and of the duration for which the crystal is annealed at that maximum temperature. The limited data prevent a rigorous determination of the functional relationships involved, but the observed behavior is generally consistent with what might be expected if the domain walls are pinned by point defects. Although these experiments demonstrate the potential of kinetic studies of memory effects associated with phase transitions, quantitative interpretations will require more data of the sort reported here.

Acknowledgments

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