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ABNORMAL INTERNAL FRICTION PEAKS IN SINGLE-CRYSTAL ICE

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A series of sharp skewed internal friction peaks were observed during warming of single-crystal ice after cooling below -120°C (153°K), the cubic-hexagonal transition temperature. The peaks were higher when the strain amplitude was lower. Since handling and annealing strongly affect the occurrence of the skewed peaks, those peaks are probably related to the stacking fault process in hexagonal-cubic transition.

INTRODUCTION

An extensive study of internal friction in single-crystal ice near 850 Hz has shown many anomalous measurements of the decrement, in our case tan δ, at temperatures below -80°C. Helmreich has reported similar anomalous behavior in the same temperature region during elastic constant measurements (1969) and later in sound velocity measurements (1972). Sugisaki et al. (1969) and Matsuo et al. (1972) have also reported anomalous heat capacity measurements in this temperature region.

This behavior is normally interpreted as an order-disorder phase transition or a cubic to hexagonal phase transformation. The results presented here are not interpreted by any theory but a hypothesis is set forth that these results also represent a cubic to hexagonal transformation.

SAMPLE PREPARATION AND EXPERIMENTAL SET-UP

The two samples used in these experiments were prepared from Mendenhall Glacier single-crystal ice, the properties of which are well-known from the X-ray topographic studies of Itagaki (1970), and the study of mechanical properties by Higashi (1969). The two samples were cut side by side from one stock crystal to obtain properties as similar as possible. The samples were oriented only with respect to the C-axis, one with the C-axis perpendicular to the plane of bending oscillation, hereafter referred to as crystal A, the other with the C-axis parallel to the plane of oscillation, hereafter referred to as crystal B.

The sample holder was redesigned following previous experiments so that the sample was held between fine, stiff wires at its oscillation nodes (Fig. 1). At the beginning of this set of experiments iron filings were made to adhere to the ends of the crystals by using a Formvar/iron filing mixture. This was changed, as indicated later, to soft iron clips that were slipped over the ends of the crystals. Both the driving and pick-up magnets were originally of the electromagnetic type as indicated in Figure 2. From the nature of the first results it appeared

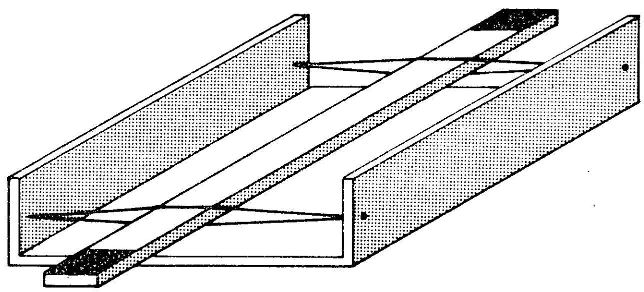

Figure 1. Sample holder.

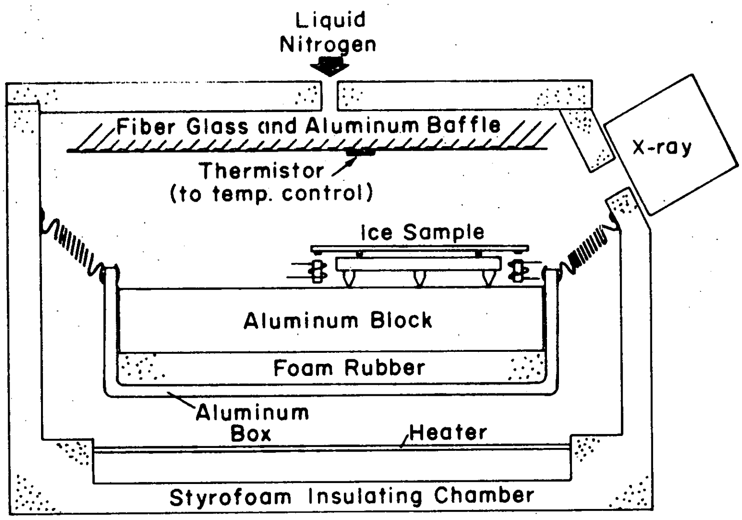

Figure 2. Measurement chamber.

that the pick-up system might be causing anomalous peaks through reduction of magnetic permeability in the magnetic circuits at lower temperature. Therefore, an acoustic pick-up (microphone) was substituted for the electromagnetic one, leaving only the driving system electromagnetic. Because of the high external acoustic sensitivity of the pick-up, a 2-inch layer of fiber glass was installed around the existing Styrofoam box. This insulation dropped the background to 3-5% of the signal level, which was sufficient to eliminate noise interference.

The sample was oscillated in the flexure mode at its natural fundamental frequency by a closed feedback system as illustrated in Figure 3. During any particular experiment of the sample the amplitude could either be maintained constant by the system or changed manually. In order to leave the sample as nearly undisturbed as possible, the temperature was sensed with a thermocouple on the surface of a dummy sample placed near the real sample. A block diagram of the complete system is shown in Figure 4. The timing and switching unit causes the system to

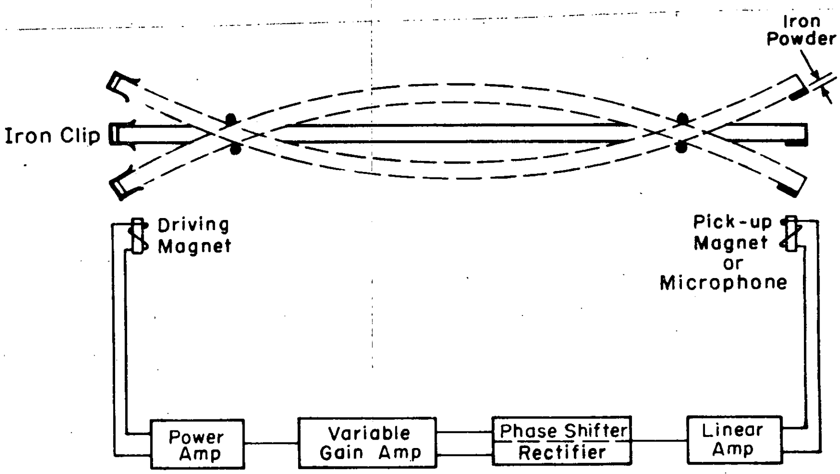

Figure 3. Closed oscillation loop.

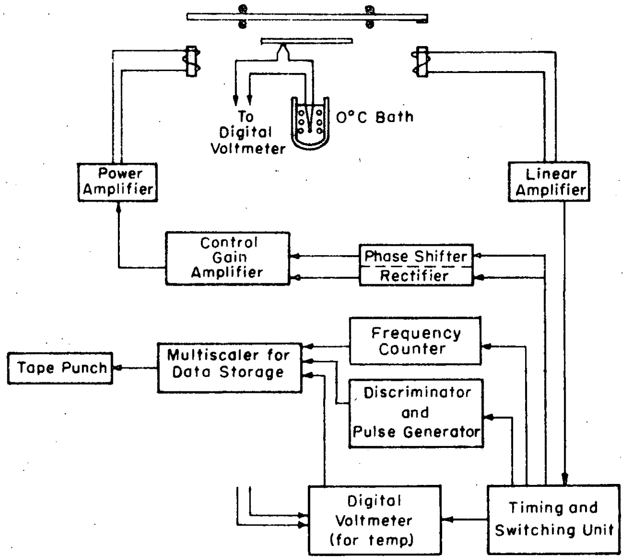

Figure 4. Block diagram of electronic system.

take one set of readings automatically every 20 seconds. Tan δ is calculated from a count of the number of oscillations needed for the amplitude to decay by a factor of one-half, as determined by the discriminator, when the closed oscillation loop is opened. A more detailed description of the whole system is given by VanDevender and Itagaki (1973).

RESULTS

Since the history of the crystal appears to be of some importance, the results will be presented chronologically. Cooling rate and strain amplitude also have an effect on the results obtained. The strain amplitude referred to below comes from a rough calculation and may be in error by as much as 50%. The relative values given, therefore, are approximations.

It has been found in recent X-ray studies that defects, particularly those produced by X-rays, have a lifetime of several weeks if the temperature of the crystal is not allowed to rise above -60°C. On the other hand, the highest temperature at which cubic ice has been observed is -70°C (Sugisaki et al. 1969). Therefore, in many of the later results presented here the temperature was only brought up to -65°C and held there until the next cooling with dry ice. Dry ice was also used to cool to this temperature range and the cooling rates were always less than 0.5 deg/min. The cooling rates given below are the rates from -60°C on down.

Crystal A was the first one used. After several days of background data were recorded at -10°C, the temperature was lowered without taking data; subsequent warming produced the curve shown in Figure 5a. This was the first time that crystal A was cooled, the rate being about 3 deg/min with a strain amplitude near 1 x 10^{-5}. This run was started three days after the crystal was prepared and it had received no harsh mechanical treatment during that period. Note the sharp skew peak around -95°C that overlaps the second peak reported by VanDevender and Itagaki (1973). Because of the nature of this skew peak, the crystal was allowed to anneal at -10°C for four days while tests were made on the system to determine the reason for this strange peak.

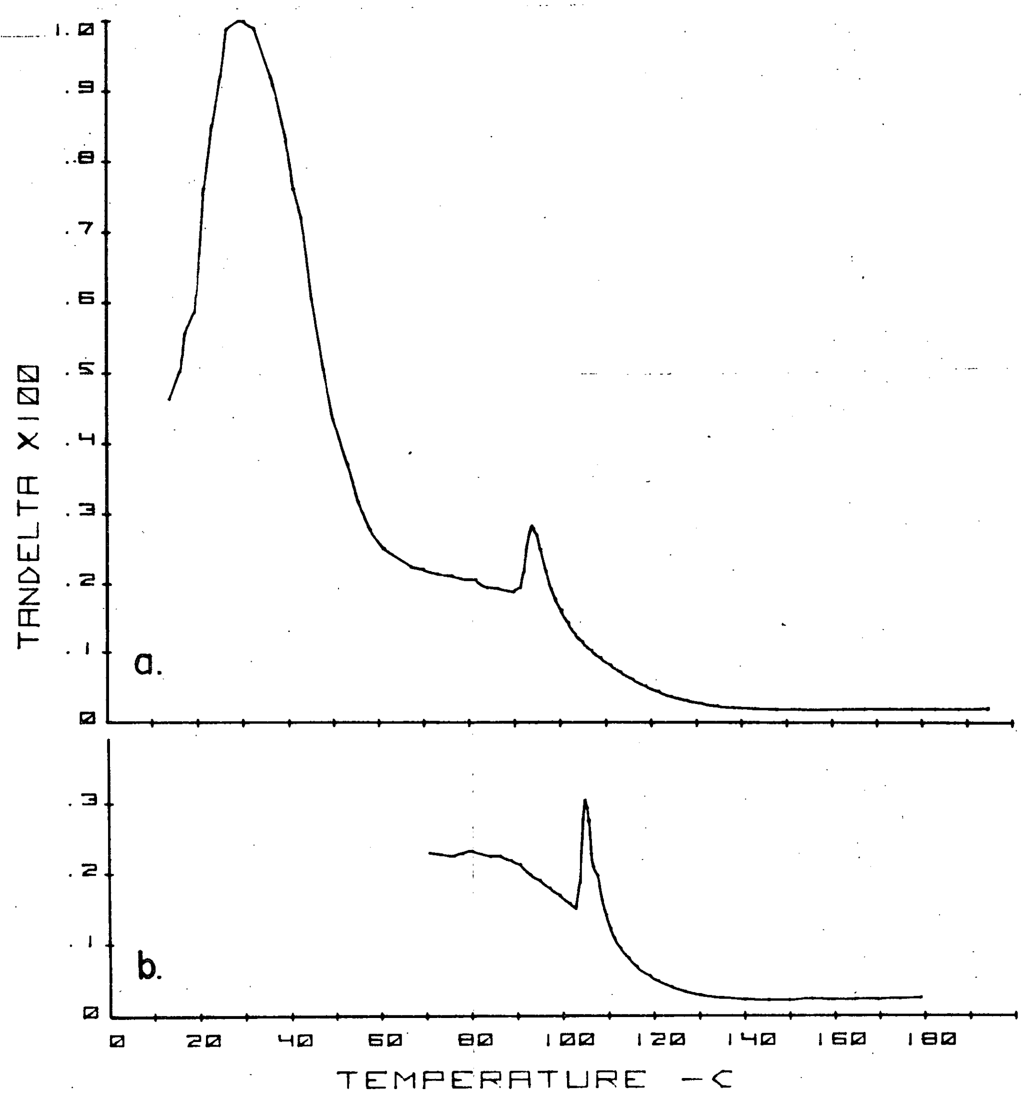

Figure 5. a. First run in which a skew peak was noticed. b. Second run, confirming the existence of a skew peak.

The experiment was attempted again, this time cooling more carefully at a rate of 2 deg/min with the other parameters the same. Figure 5b shows the result: a skew peak very similar to the first one was reproduced, but at a lower temperature. The warming run was halted at -65°C and the crystal left oscillating there for constant temperature X-ray study. During the next three days the crystal was exposed to X-irradiation at -78°C three separate times for a total of four hours. This irradiation increased the tan δ maximum of the second peak and shifted this maximum from -79°C to -72°C. To determine the effect of this irradiation on the skew peak, the temperature was lowered at a rate of 2 deg/min immediately after the last irradiation. In the subsequent warming curve (Fig. 6a) the main skew peak remained, along with a few other irregularities. Crystal A was annealed again at -10°C for three days, and after similar treatment, with a total of 15 hours of irradiation prior to the run, a curve similar to that in Figure 6a was obtained. This crystal was then retired and left to anneal at rest at -10°C.

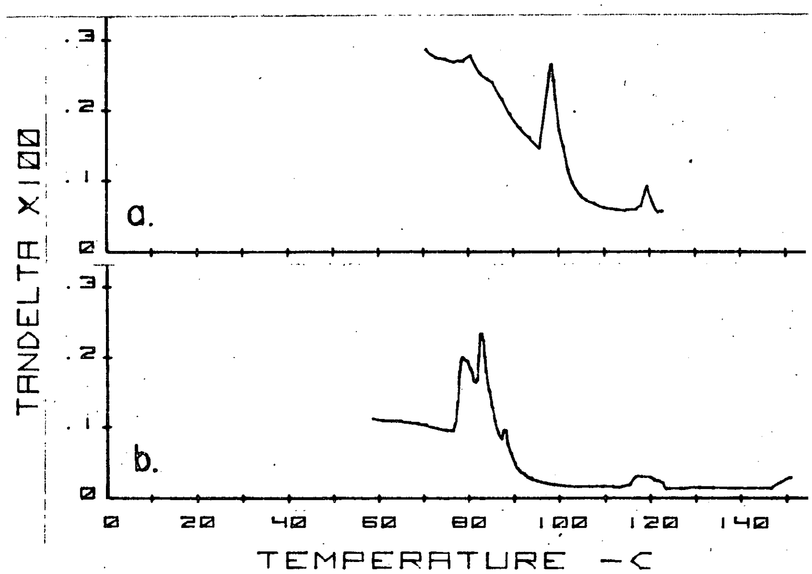

Figure 6. a. Skew peak area after 4 hours of X-irradiation. b. First appearance of skew peak in crystal oriented parallel to the plane of oscillation.

In order to check the effect of orientation on this newly found skew peak, crystal B was cut at a 90° angle to the first. System problems caused this crystal to be handled a little more before any reliable data were obtained. This may be the reason for the broader, more structured skew peak found in the first warming curve of this crystal (Fig. 6b). The cooling rate and strain amplitude for this initial run were similar to those at which the skew peak occurred in the previous crystal, i.e. 2 deg/min and 1 x 10^{-5}.

Additional runs reproduced the results but there seemed to be more scatter than desired. After some time it was found that the iron filings were coming loose and forming a fine bridge between the pick-up magnet and the crystal. This problem was solved by replacing the iron filings with iron clips as shown in Figure 3. There were six cooling-warming cycles during this testing period and they started to show some amplitude dependency. However, the data were not too reliable so an amplitude dependency series was initiated after the iron clips were installed.

Crystal B underwent some handling during the test period described above so it was allowed to anneal for 5 days at $-10^{\circ}C$. On the 34th day after preparation, the amplitude dependency series began. The cooling rates for all three runs were the same, 1 deg/min, but the strain amplitude was changed from 1×10^{-5} to 5×10^{-6} then to 3.8×10^{-6}. The warming curves are shown in Figure 7. The first thing to notice is the greater

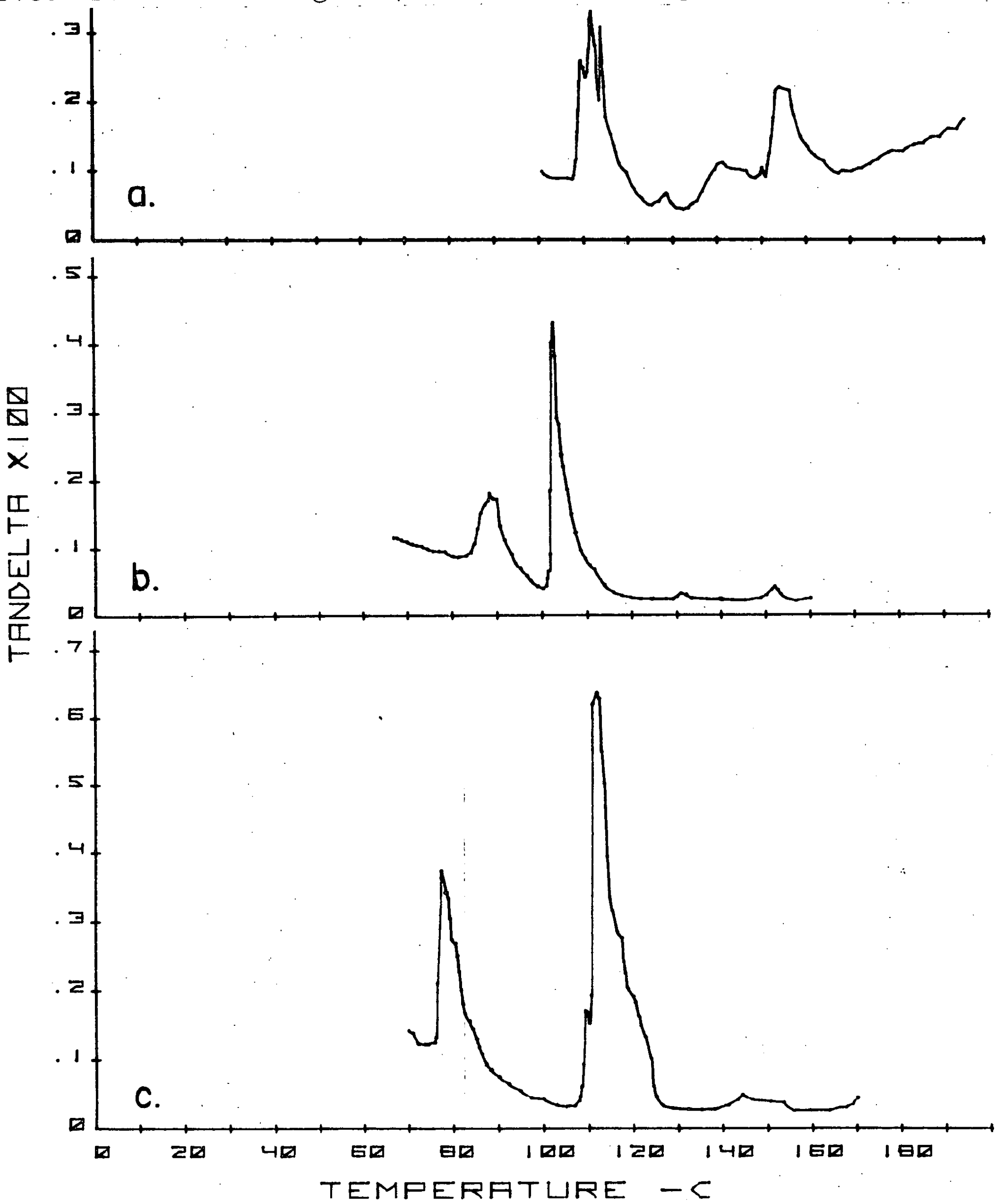

Figure 7. Strain amplitude comparison results.

amount of noise and other damping factors contributing to the roughness of the lower temperature part of the curve when the strain amplitude was high. If the peak height of the largest skew peak in each of these runs is compared to the value of tan δ at that same temperature during cooling, the ratios are 10:1, 27:1 and 33:1 respectively, top to bottom. The cooling curve associated with the medium amplitude run is shown in Figure 8a. It is typical of many of the cooling curves having small, sharp peaks. Some curves had very small, smooth bumps, while others were just smooth or a combination of peaks and bumps.

After the amplitude comparison series, the crystal was annealed at rest at -10°C for 16 days. Before the X-ray effect was checked, a base run was taken. The cooling rate was again 1 deg/min and the medium amplitude, 5×10^{-6}, was chosen. The results were similar to the previous run at this amplitude except that the peak height ratio decreased to 16:1.

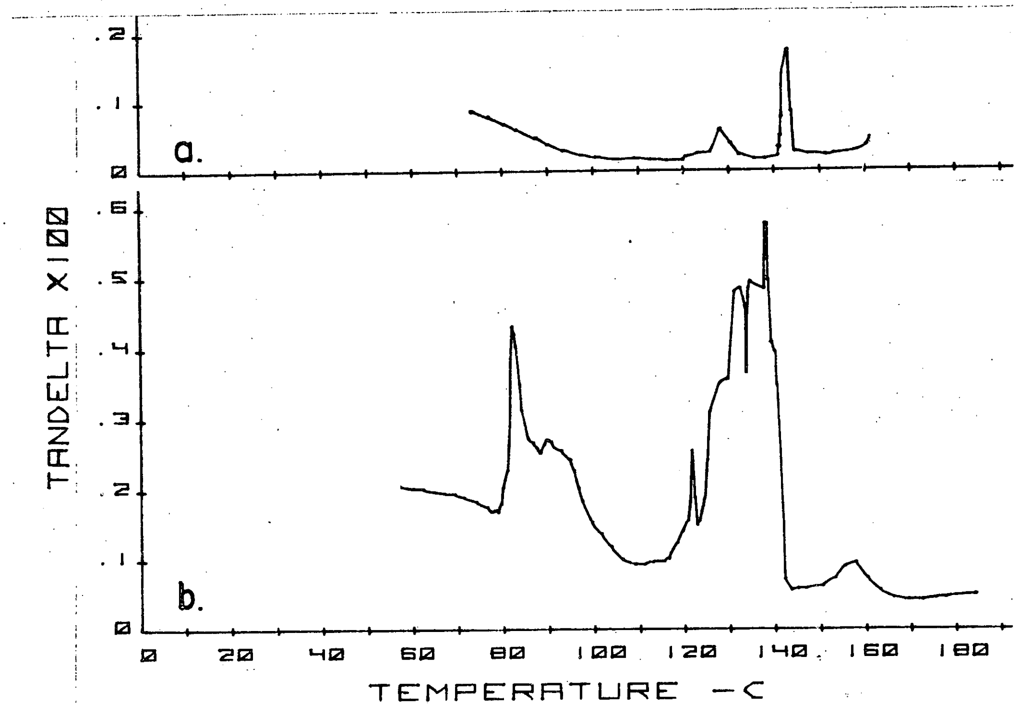

Figure 8. a. Normal cooling curve. b. Effect of X-irradiation for 30 minutes at -180°C.

It was thought that X-irradiation might reveal the causes that were producing the skew peaks so the temperature of the crystal was lowered to -180°C and held there for 30 minutes with the X-ray on. The crystal was then allowed to warm with the X-ray off; the curve shown in Figure 8b was the result.

Because of mechanical problems it was decided to try an acoustic pick-up. The first run with this new system showed a definite need for more acoustic isolation. The additional insulation previously described was then provided.

In the next series of runs an attempt was made to establish a triggering temperature for this phenomenon. The crystal was cooled from -65°C first to -100°C then to -110°C and so on. The cooling rate throughout this series was 0.5 deg/min and the strain amplitude was 5×10^{-6} for all runs. The first part of this series is shown in Figure 9. Warming curves a and b from -100°C and -110°C respectively

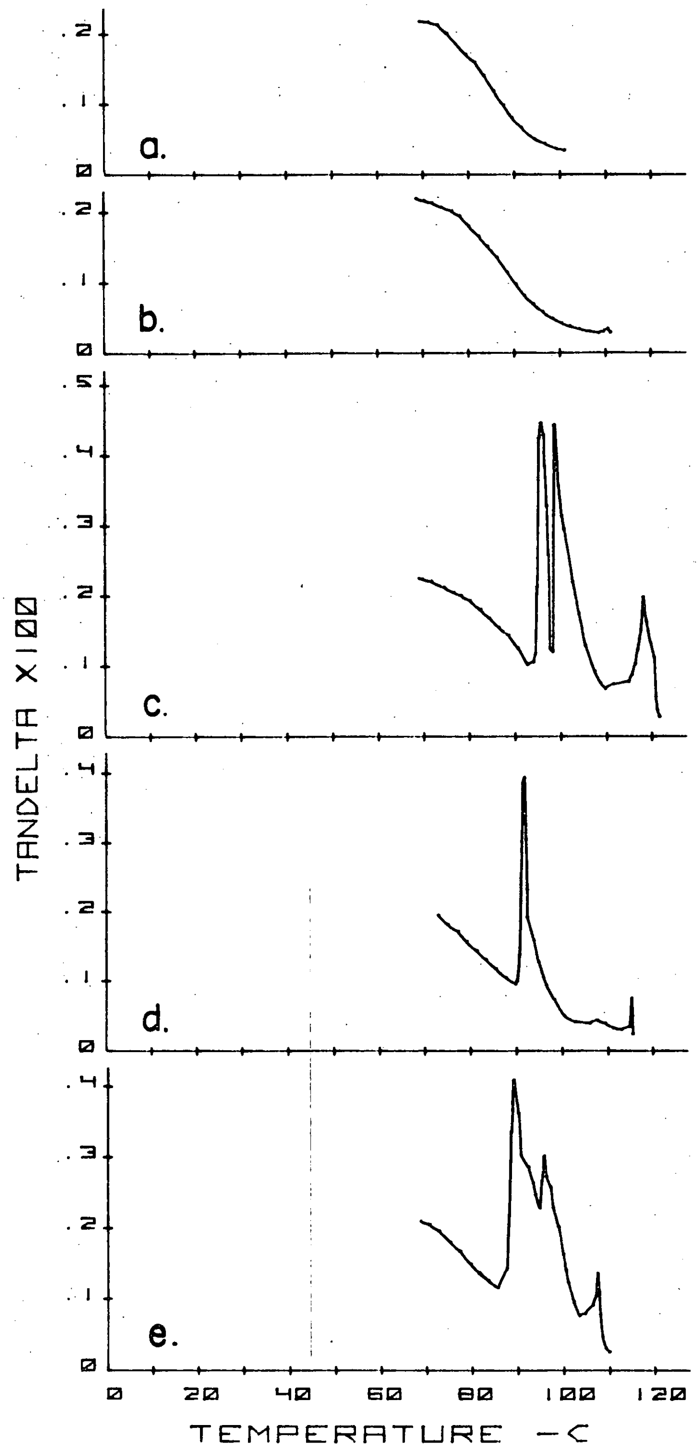

Figure 9. Triggering temperature series (part 1); warming curves.

show very little effect. However, in warming curve c, from -120°C, it can be seen that the mechanism has been triggered and several skew peaks exist. Warming curves d and e, from -115°C and -110°C again, have skew peaks, with the latter being quite broad. The second part of this series is shown in Figure 10, with curve a being a typical cooling curve for the whole series. None of the cooling curves had any irregularities. The crystal accidentally warmed up to -20°C overnight so the effects of this short low temperature annealing were recorded in another run to -110°C as shown in Figure 10b. To eliminate the mechanical strain effect during cooling, the crystal was cooled at rest to -120°C, but as seen in Figure 10c the mechanism was still triggered. This crystal was then retired to anneal at rest at -10°C and crystal A was subjected to a similar triggering temperature series.

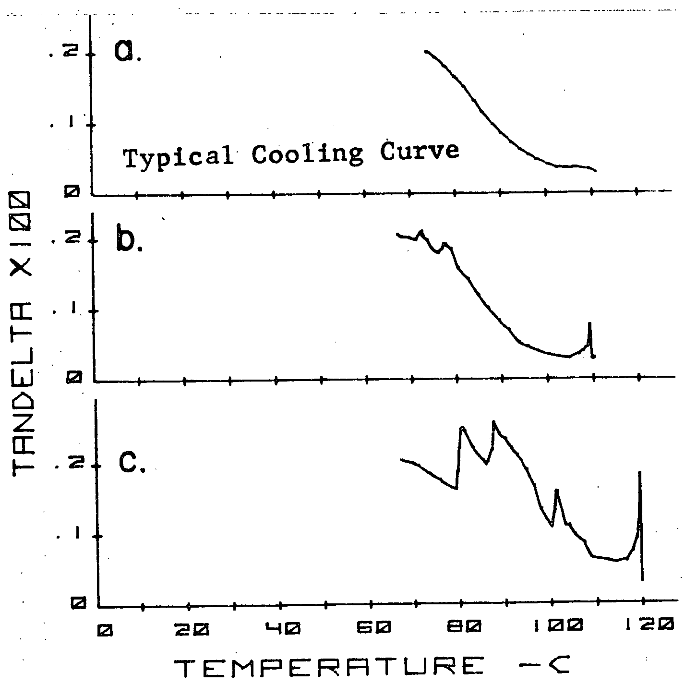

Figure 10. Triggering temperatures series (part 2).

This crystal had been annealing for 105 days. To test the system under the original conditions, the iron filings previously attached were not removed at this time. The series was handled in the same manner, with cooling rates on the order of 0.5 deg/min and strain amplitudes of 5×10^{-6}. Again the crystal was cooled from -65°C, first to -100°C, then -110°C, -120°C, -130°C, -150°C and finally -175°C. Because all the results showed smooth warming curves, only some of these runs are shown in Figure 11. Curves a and b, from -100°C and -120°C respectively, show almost no anomalies. The cooling and warming curves of one run are reproduced on a single set of axes (Fig. 11c) with the cooling curve shown by a dashed line. The cooling curve shows a slight shoulder near -90°C but otherwise follows the same path as the warming curve. Figure 11d is the warming curve from -175°C, still with no skew peaks.

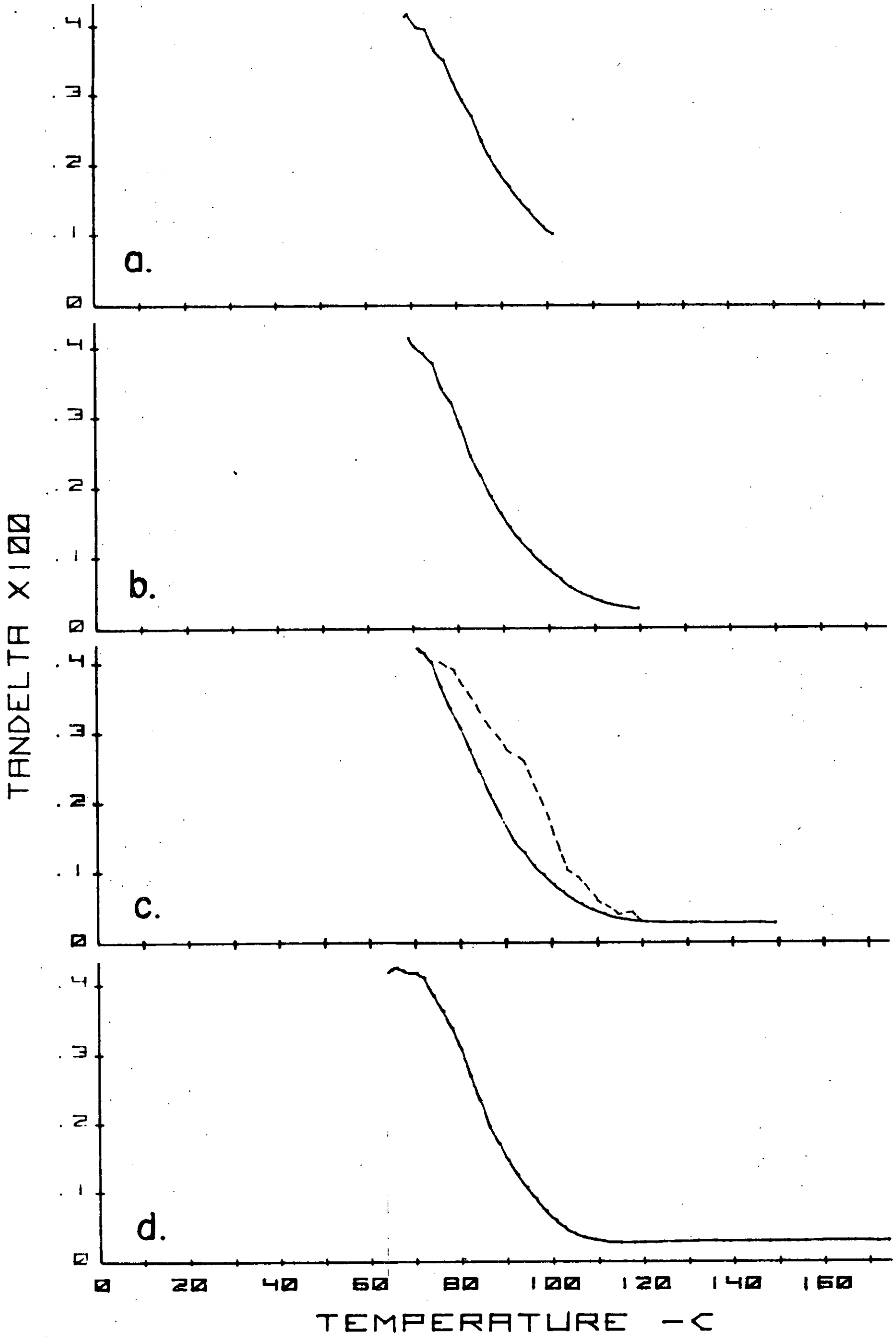

Figure 11. Triggering temperature series for crystal with C-axis perpendicular to the plane of oscillation.

Since no skew peaks were found in the above series, the spring clips were installed on crystal A after an additional annealing period of 28 days. A subsequent warming curve (Fig. 12a) from -140°C shows some sort of skew peak. Another run to confirm the existence of the peak shows a more well-defined skew peak (Fig. 12b). In these last two runs the cooling rate was somewhat higher than the previous series, 1 deg/min and 2 deg/min respectively. The strain amplitude was also raised to 1×10^{-5}.

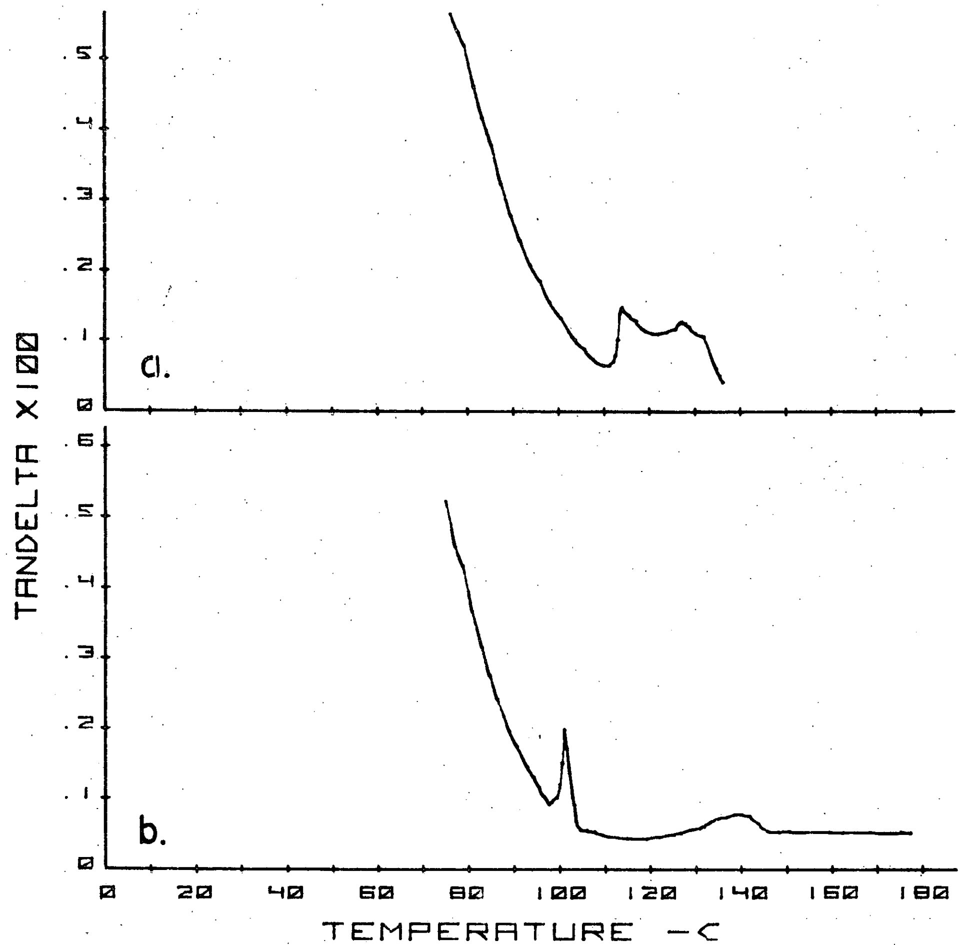

Figure 12. a. First occurrence of skew peak after annealing. b. Last run with perpendicular orientation.

Crystal B was tested again after annealing for 49 days to see if the skew peaks would reoccur in a warming curve. It was cooled carefully at a rate of 0.5 deg/min to -125°C with a strain amplitude of 5×10^{-6}. Even under these conditions the mechanism was triggered in this crystal, as seen in the warming curve (Fig. 13).

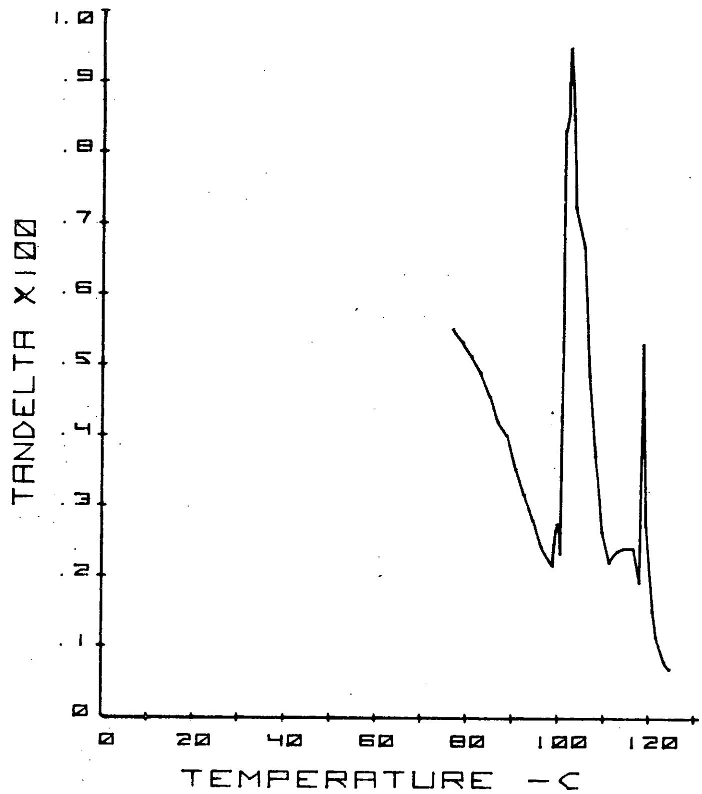

Figure 13. Final run of crystal with C-axis oriented parallel.

DISCUSSION

Although the results seem complicated, several facts can be stated:

1. Straining due to mechanical handling and thermal stressing causes broadened, more structured skew peaks.

2. X-ray irradiation makes skew peaks more pronounced and structured.

3. Once a skew peak is triggered by cooling beyond a certain point, it persists, even at higher temperatures.

4. Skew peaks are higher when the strain amplitude is smaller or the rate of cooling is higher, as shown in Figure 14.

5. The peak temperature becomes higher as the strain amplitude becomes lower.

6. The peak disappears after prolonged annealing.

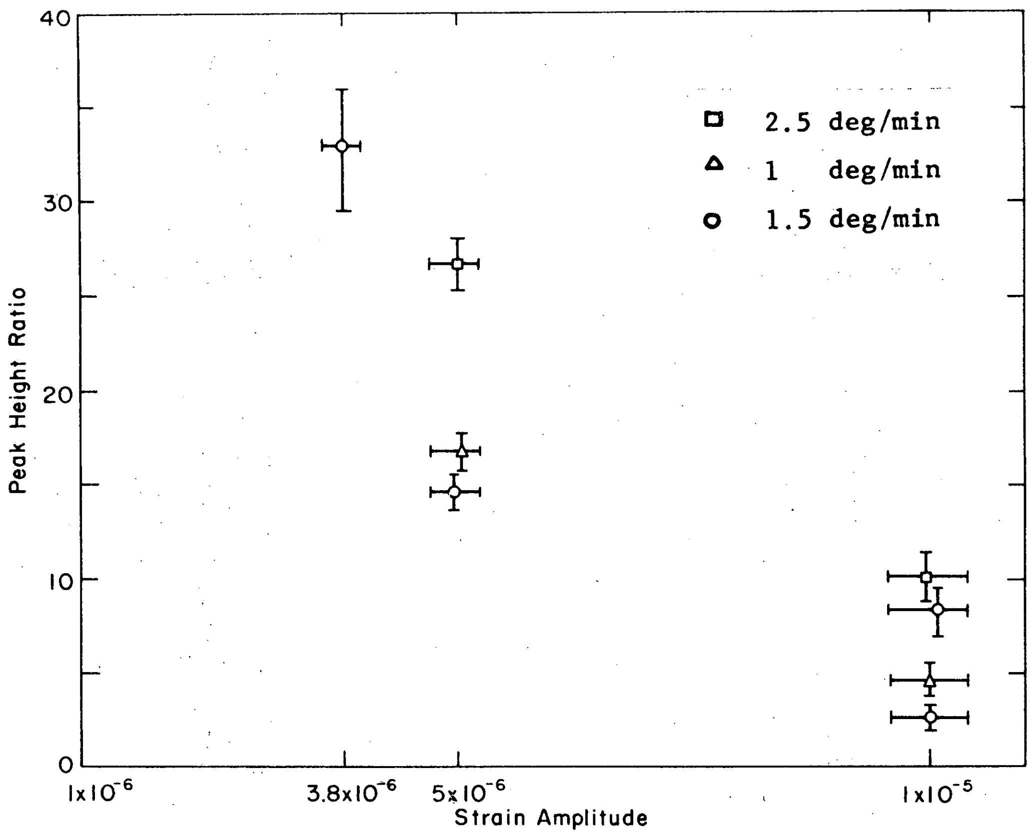

Figure 14.

These facts indicate that the skew peaks originate through some structure-sensitive defect such as a dislocation. One process that could possibly be involved in the development of skew peaks is hexagonal-cubic transition of ice I. The hexagonal system has a stacking sequence of A-B-A-B while the cubic system has a stacking sequence of A-B-C-A-B-C. We can treat the hexagonal system as a cubic system with a C-type layer stacking fault each two layers or vice versa. Creation or annihilation of these stacking faults would require an energy supply until a lower energy state crystallographic system (hexagonal for higher temperature, cubic for lower temperature) grew large enough to supply the energy for transformation by itself.

The ideas set forth above are only speculation as there is no firm evidence to base them on. It seems that defect density is the major contributing factor to the phenomenon presented in this paper. Particular defects such as partial dislocations and stacking faults are important in phase transformations (Hirth and Lothe 1968). The relaxations associated with such phase transformations are discussed in some detail by Nowick and Berry (1972) but the character of these data doesn't easily fit a single theory.

Although the properties of these crystals are well known it is not very well known just what the local situation in a particular crystal is. The phenomenon observed here must be more of a localized phase transformation than a complete change of the entire crystal. Therefore, if the proper set of defects is within a local area, a change in the stacking sequence from hexagonal to cubic could be initiated by the thermal strain caused by the temperature gradient within the crystal and/or the mechanical strain applied.

Since the process is related to stacking fault generation, and the temperature range coincided with the known transition temperature (for listing see Sugisaki et al. 1969) this speculation has some basis though the details of the process are open to future study.

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