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PROGRESS REPORT

Period May 22, 1974 through July 21, 1974

INVESTIGATION OF CRYSTAL GROWTH FROM SOLUTIONS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
CONTRACT NUMBER NAS 8-28098

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Project Director
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University, Alabama 35486 August 7, 1974

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I. Progress During Reported Period

A. Introduction

The effects of convection on crystal growth have been actively studied by many workers, especially for the case of metal crystals.[1] Some effort has also been made by our group at UAT to understand the effect of convection in solution crystal growth.[2] Our group has found that convection degrades the quality of the resulting crystal. Thus we suggested that if a crystal were grown from solution placed in a zero-gravity environment, the quality of the resulting crystal should be extremely high. For this reason a crystal of Rochelle salt was actually grown on Skylab-4 and the quality of the recovered crystal was investigated. The code number of this experiment is TV-105, and Astronaut Col. Pogue performed it.

B. Summary

The crystal of Rochelle salt grown on board Skylab-4 has the following unique features: (i) the typical cavity is a long tube extending along the c-axis, the average length being 4mm, compared to 0.1mm that is the average size in the case of earth-grown crystals; (ii) the crystal consists of several single crystals, the corresponding axes of which are parallel to each other. In addition, a preliminary measurement was made on the ferroelectric hysteresis curve of this Rochelle salt crystal.

C. Ground-Based Preparation

Details of the ground-based preparations are given elsewhere.[3] The Rochelle salt chemical used was supplied by J. T. Baker Chemical Company.

The large seed crystals for this experiment were grown by slow cooling techniques. Granular Rochelle salt used for this experiment was prepared by slowly cooling a saturated solution and afterwards was dried over filter papers.

The solution used for the experiment was saturated at 25°C.

A seed crystal and granular Rochelle salt, their combined weight being 30 grams, were placed in a Skylab food can and filled with saturated solution. This food can was heated under conditions similar to those found in a Skylab food tray. It was determined that 40 minutes after the heater was turned on, the granular Rochelle salt dissolved completely, but a portion of the seed crystal remained undissolved. Thus it was suggested that the optimum heating time was 40 minutes.

The material actually supplied for the flight experiment is as follows:

seed	21.6 grams
granular Rochelle salt	8.4 grams
Sum	30.0 grams,

and a Rochelle salt solution saturated at 25°C.

Details of the canning procedure will be given in the Mission Report which is being prepared by Mr. Tommy Bannister.

D. Summary of the Flight Experiment

Details of the flight experiment are given in the Mission Report indicated in the preceeding section.

The sealed food can with Rochelle salt mixture supplied was heated to about 65°C for about 40 minutes in one of the units of the food tray, then slowly cooled to ambient cabin temperature. We estimate the cooling process took 5-10 hours, and the initial growth period was about 48 hours. After approximately 30 more days of growth time the can was opened and the resulting solid material was recovered.

The following list of materials was returned to the PI at UAT:

1. Film Serial SL4-502, Title-Skylab-4
   DAY004, TV-105

2. TV-105 Color Prints
   SL4-146-4894 through 4896 and SL4-148-5018 through 5020

3. 35 mm slides, H-02547-H

4. Voice record MC1706, MC1787-1, and MC1787-2

5. Rochelle salt crystal and wipes used to dry it after recovery.

The 16 mm film clip shows Col Pogue beginning to heat the food can with Rochelle salt and saturated solution. The color prints and the 35 mm slides show the food can during the experiment and the Rochelle salt crystal that was recovered.

E. Observations

1. Recovered Crystal

The recovered solid consists of three relatively large crystals (see the upper photograph of Fig. 1A) whose weights are

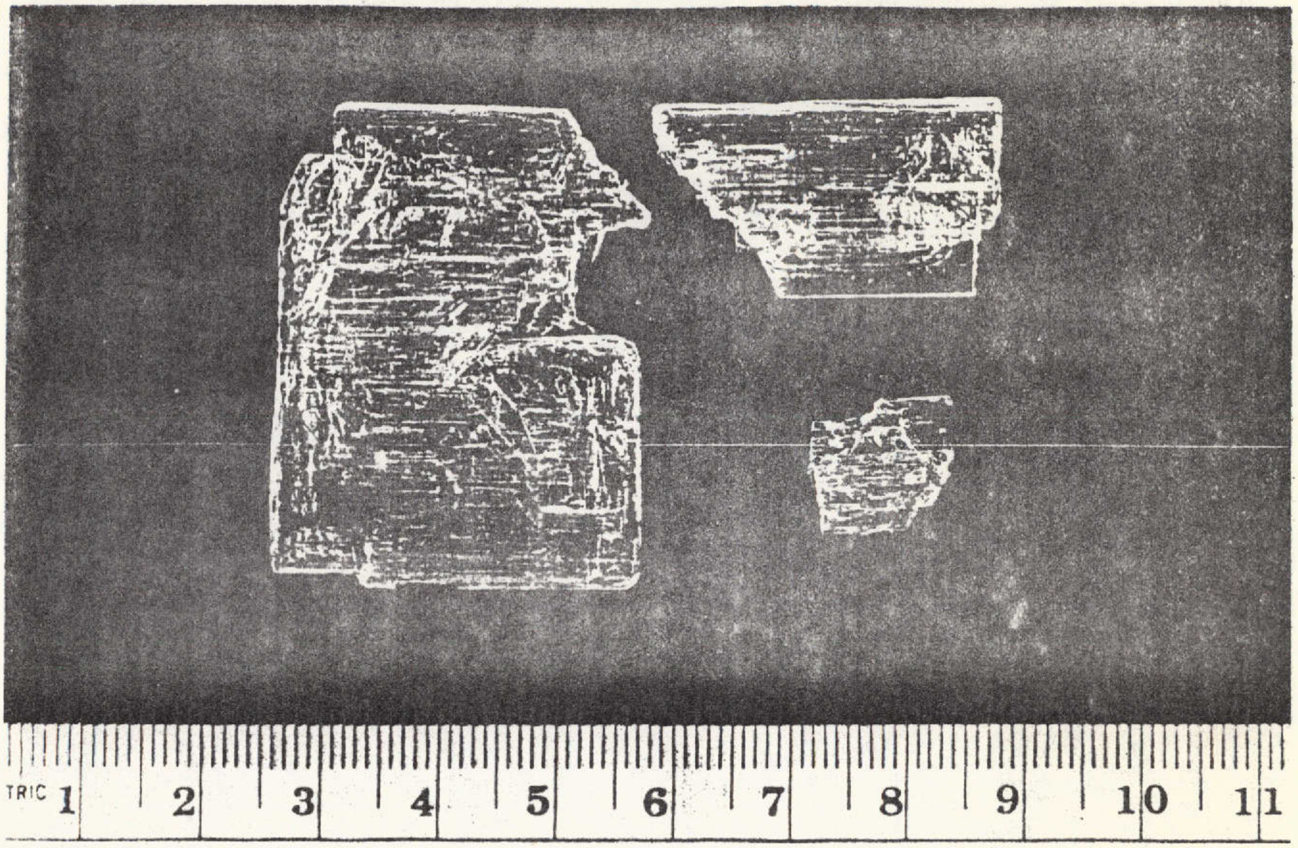
the largest #1	8.73 grams,
medium #2	2.82 grams,
the smallest #3	0.50 grams.

In addition, 16 small crystals each of which is 2 mm on a side or less were obtained. Thus, the total weight is about 12 grams, which is less than the expected weight of 30 grams. One possible explanation for this small amount of recovered product is that because of the lack of convection currents the dissolved Rochelle salt molecules reached the surface of the growing crystal very slowly, since the only transport process was diffusion. Thus, even after 30 days of growth time, the solution was still supersaturated. Supporting evidence for this explanation is the "slush" or "ice cream salt" the astronaut reported when he opened the food can to recover the crystal. This shows that the solution was still supersaturated when it was opened.

The crystal originally precipitated in the cabin is believed to be one single crystal. The lower photograph of Fig. 1A shows the three crystals #1-3 assembled into one large crystal. This conclusion was further confirmed

Figure 1A.

The upper photograph shows the three largest crystals of TV-105. The lower photograph shows the same crystals assembled into one body.



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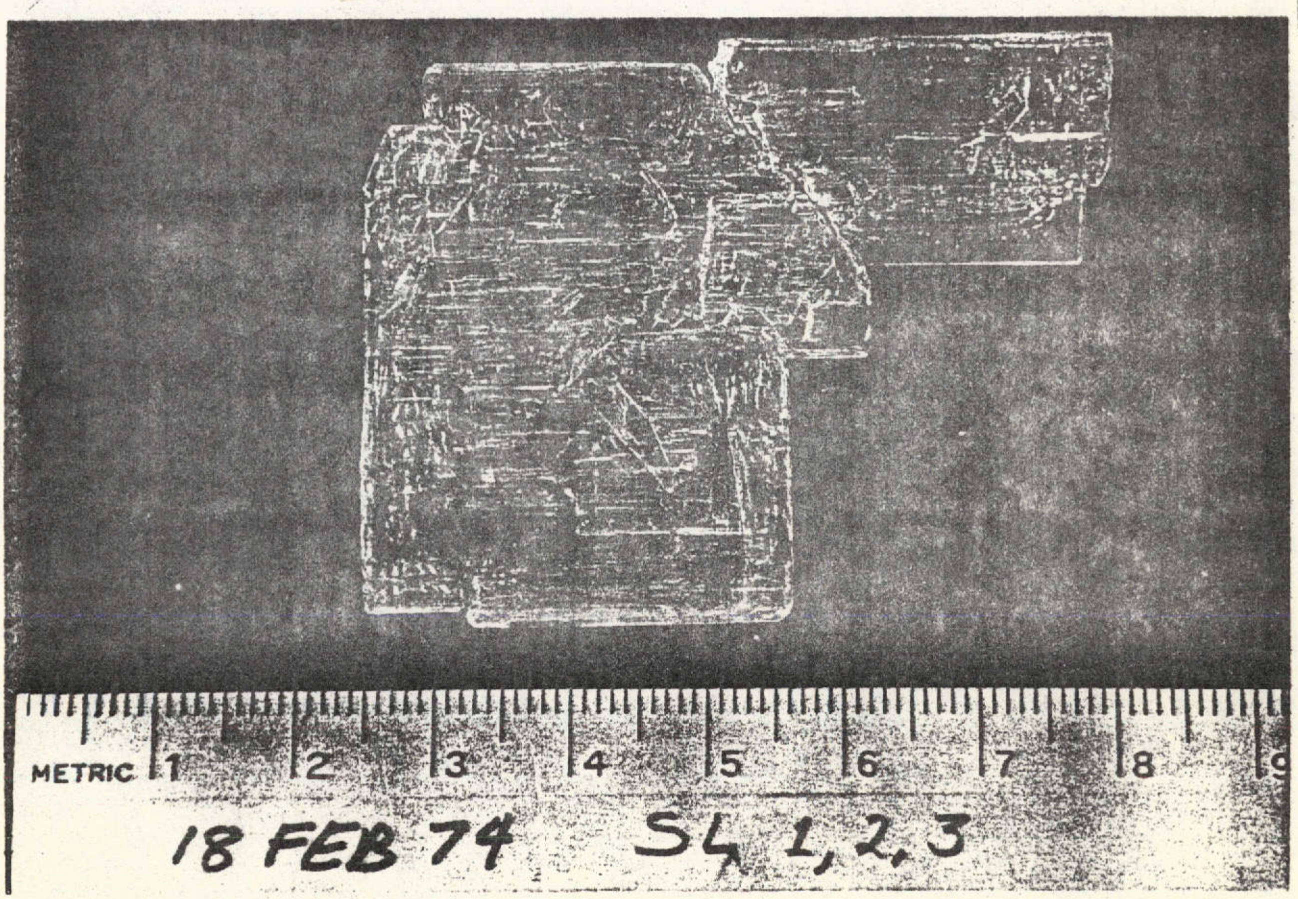

Figure 1B.

In this copy of a photograph Col. Pogue made on Skylab-4, it is clear that the original crystal was one unit. Compare this photograph to the lower picture in Fig. 1A.

5-a

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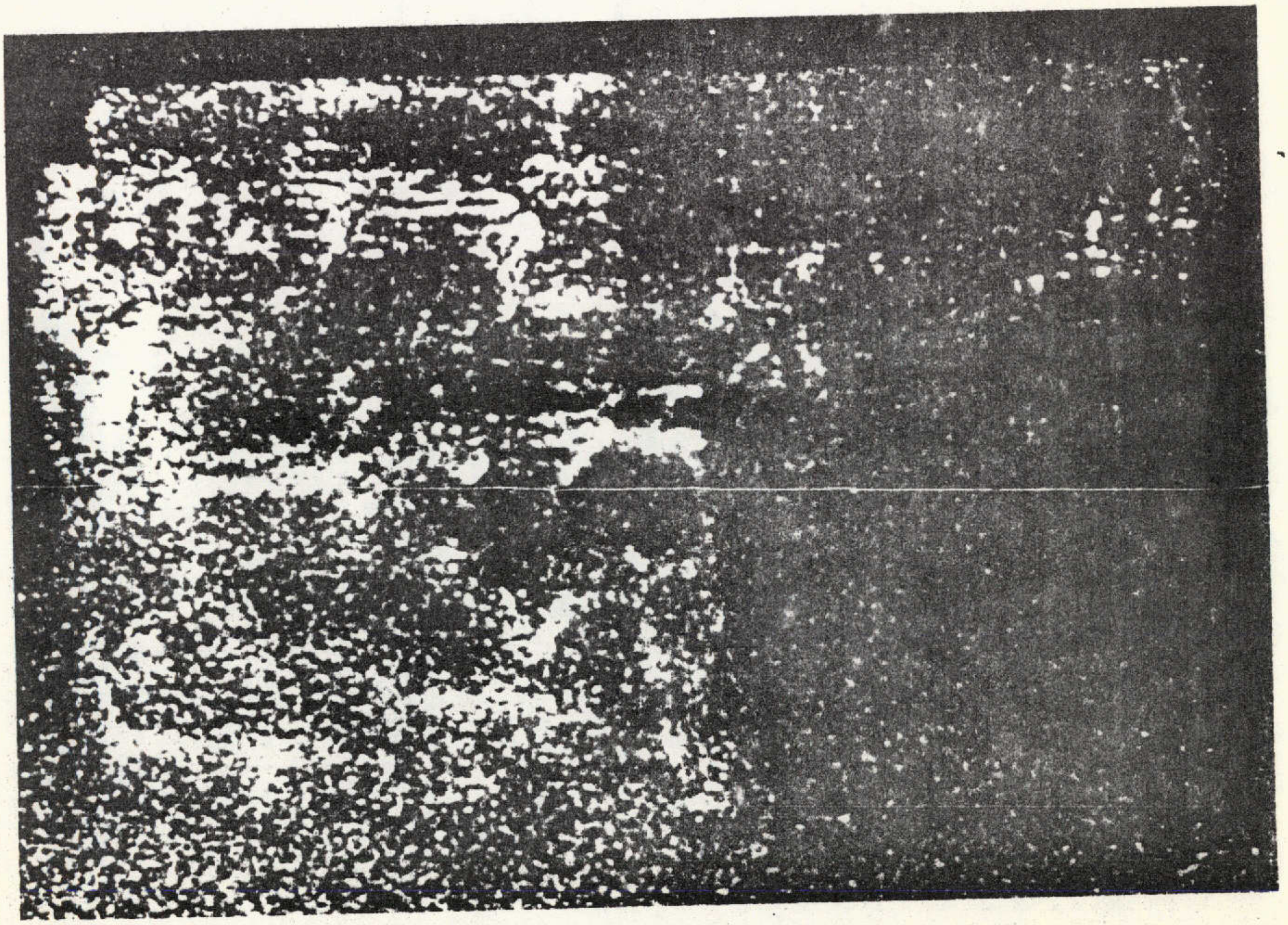


by a photograph taken by Col. Pogue (see Fig. 1B). Thus, most of the other small crystals, if not all of them, probably appeared when the big crystal was broken. The breaking of the large crystal probably occurred during re-entry or splash-down of the module.

The crystal grown on board Skylab-4 is actually a collection of at least five single crystals as is shown in Fig. 2 and 3. One very unusual thing about this collection of crystals is that the a, b, and c crystal axes of all the component crystals are parallel or very nearly parallel to each other. The crystal axes are identified in Fig. 3(A) and 3(B).

2. Macroscopic and Microscopic Defects

Most of the crystal has many defects and is not good optically, but some parts of the crystal are almost completely free of defects and appear extremely good optically.

Figure 4 shows microscope photographs of the #2 crystal and an earth-grown crystal for comparison. One can see that the cavities in the #2 crystal are highly regular compared to those in the earth-grown crystal. A typical length for a cavity in the #2 crystal was found to be 4 mm. The cavities shown in Fig. 4 have their long axes in the direction of the c crystal axis. Almost all the defects in the crystals returned from Skylab-4 are tubes elongated in this way. There are a few spheres of solution trapped in the long tubular cavities; but the spheres present are small, taking up only a fraction of the cavity volume. The extremely small diameter-to-length ratio is rarely found for cavities in earth-grown crystals.

3. Ferroelectric Quality: S-Value

The crystal returned from Skylab-4 was found to be mechanically very fragile. Thus it was concluded that slicing it by any currently available technique would probably ruin this precious crystal. For this reason we attempted to observe the preliminary hysteresis curve of this sample without slicing it.

Figure 2.

Photograph of the second largest crystal (#2). The c-axis, that is the fastest growth direction, is approximately perpendicular to the photograph plane.

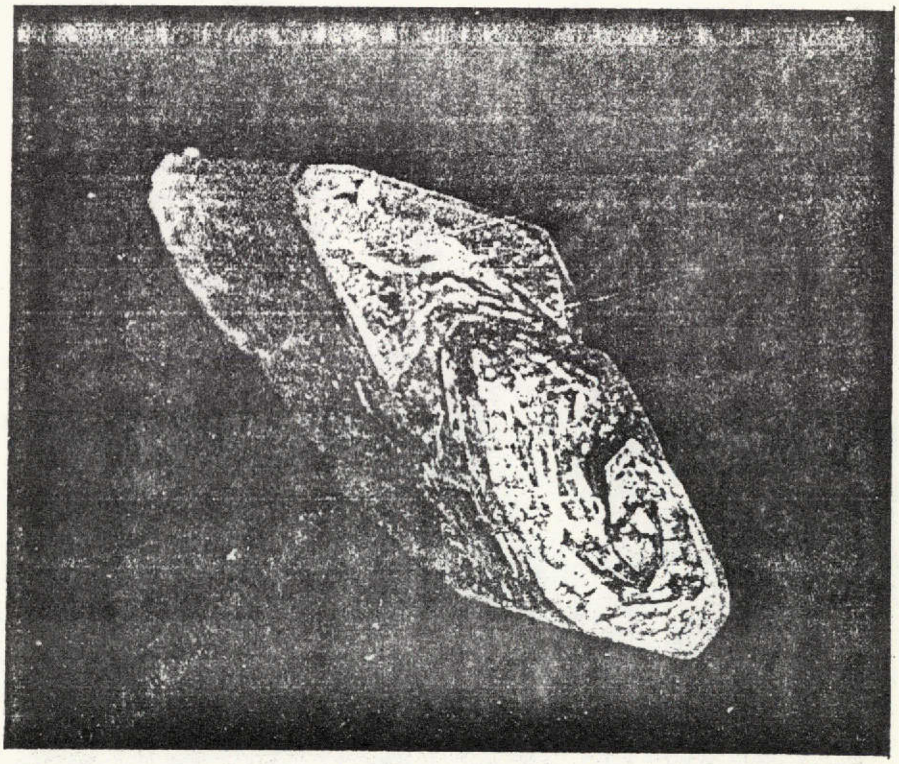
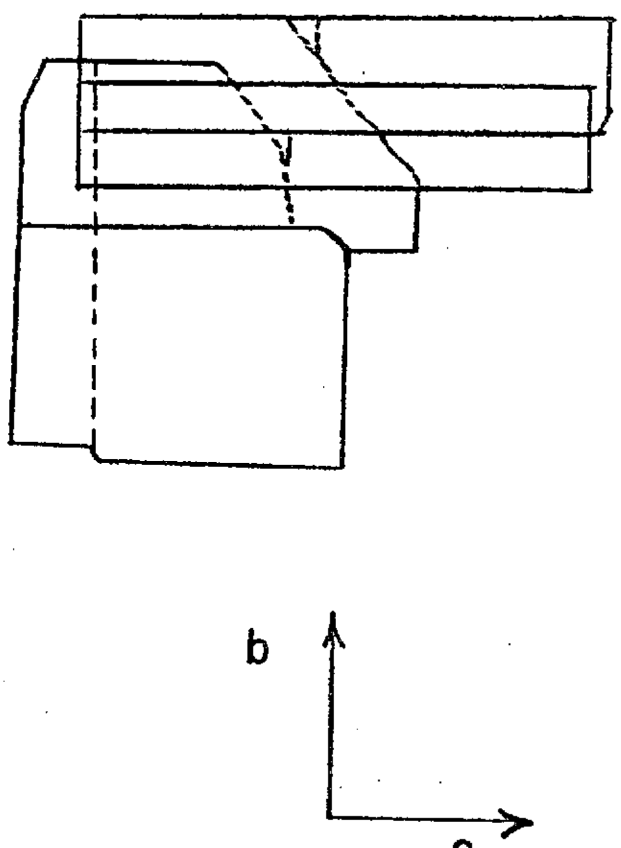


Figure 3.

Illustrations of the photographs: (A) for the lower photograph in Fig. 1, (B) for the photograph in Fig. 2. Both illustrations show that the crystal consists of several single crystals; the crystal axes are also shown.

Figure 3(A)



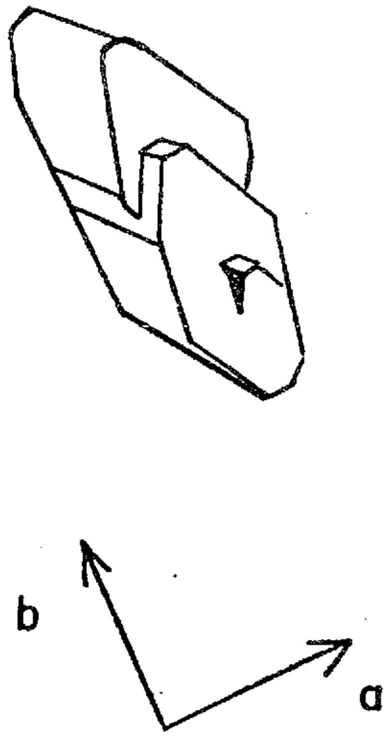


Figure 3(B)

Figure 4. Microscope Photographs.

The upper photograph is from the #2 Skylab crystal. The lower one is from an earth-grown crystal. The magnification is approximately 100.

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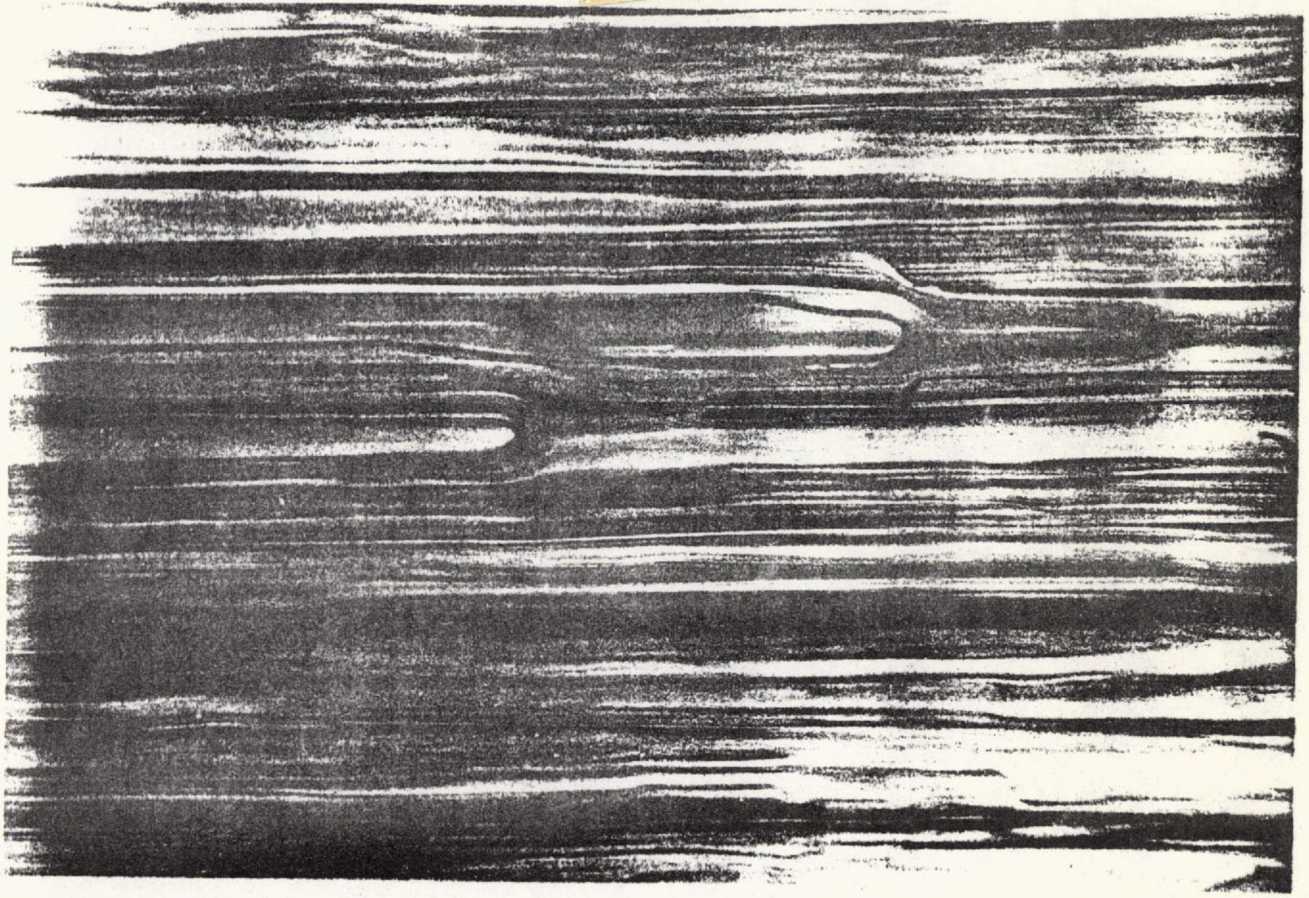

Several sets of electrodes were constructed and tested on earth-grown crystals of the same size and the most satisfactory results were obtained from the system shown in Fig. 5. Because of the high voltages necessary for this thickness (0.5 cm) of crystal, some of the circuit parameters in the capacitance bridge were also changed.

The hysteresis curve for TV-105 is given in the lower photograph of Fig. 6. The hysteresis curve for an earth-grown crystal of about the same size and thickness is shown in the upper photograph of Fig. 6, for comparison. The S-value was calculated from these curves to be 2.69 for the earth-grown crystal and 1.36 for the Skylab crystal.

The S-value, which has been defined previously,[2] is one factor which characterizes ferroelectric quality. High S-values usually indicate uniform domain structure and hence better ferroelectric qualities. The low S-value observed for the Skylab crystal seems to indicate "poor" ferroelectric quality. However, we believe that this conclusion is premature for the following reason; we used the bulk crystal for the hysteresis measurement and it has many empty microscopic cavities as is shown in Fig. 4. It is probable that even if the domain structure were uniform, the presence of the many microscopic cavities would lower the S-value, as will be explained below.

The possibility indicated above can be understood by the following simple example; consider two identical capacitors, both filled with the same dielectric material but one having a gap (see Fig. 7). The electric field in the completely filled capacitor is given by

$$E_0 = \frac{V_0}{d} .$$

Figure 5A. Drawing of System for Hysteresis Observation.

The crystal is held in place on the thermometer bulb with modeling clay. The wire electrodes are attached to the crystal surface by conductive silver paint.

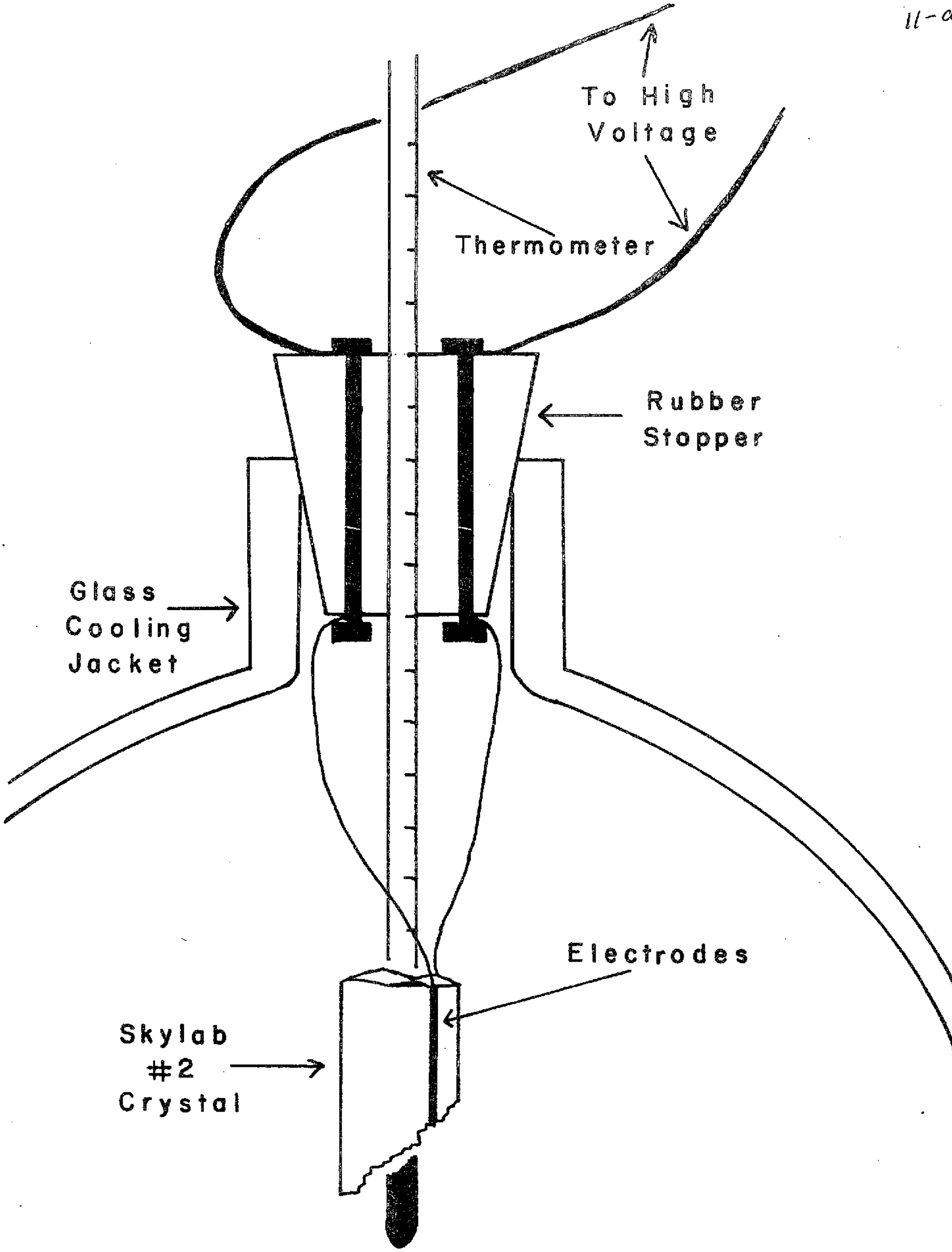
To High
Voltage
Thermometer
Rubber
Stopper
Glass
Cooling
Jacket
Electrodes
Skylab
#2
Crystal

Figure 5B. Photograph of Hysteresis Electrodes.

In this picture, the electrodes and their arrangement on a Rochelle salt crystal are shown.

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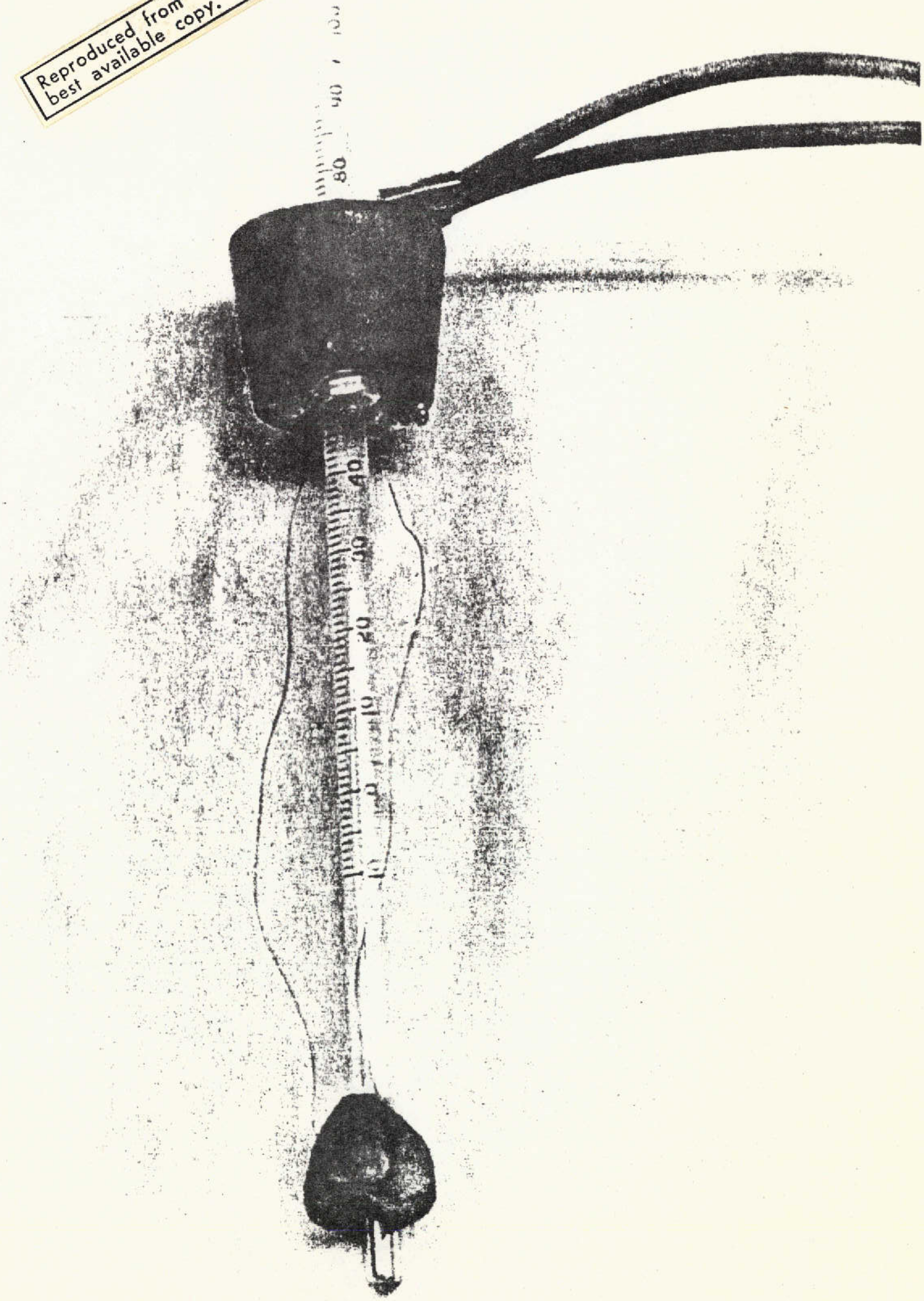
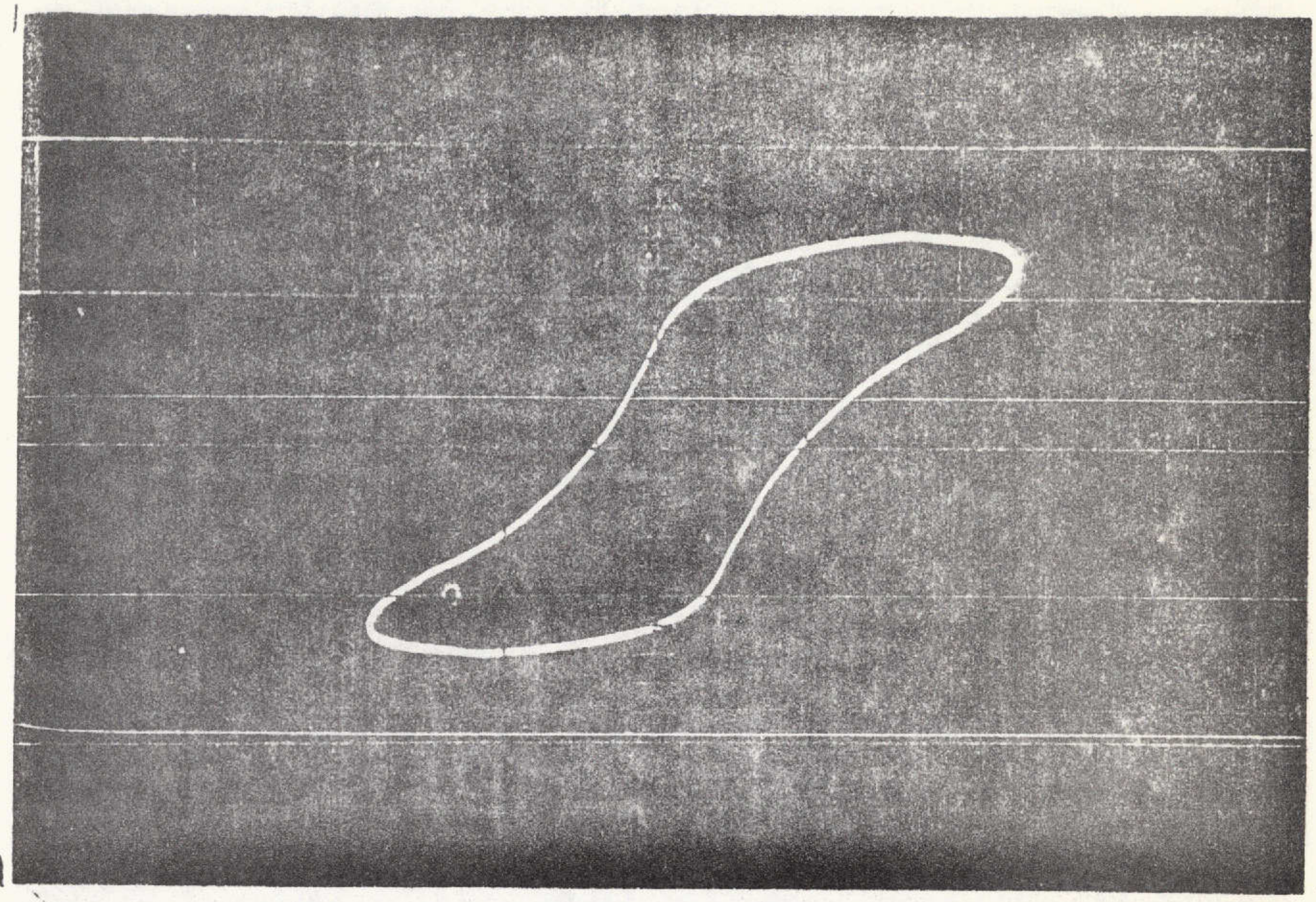


Figure 6. Hysteresis Curves.

The upper curve is from a large good-quality earth-grown crystal. The lower one is from Skylab crystal #2.



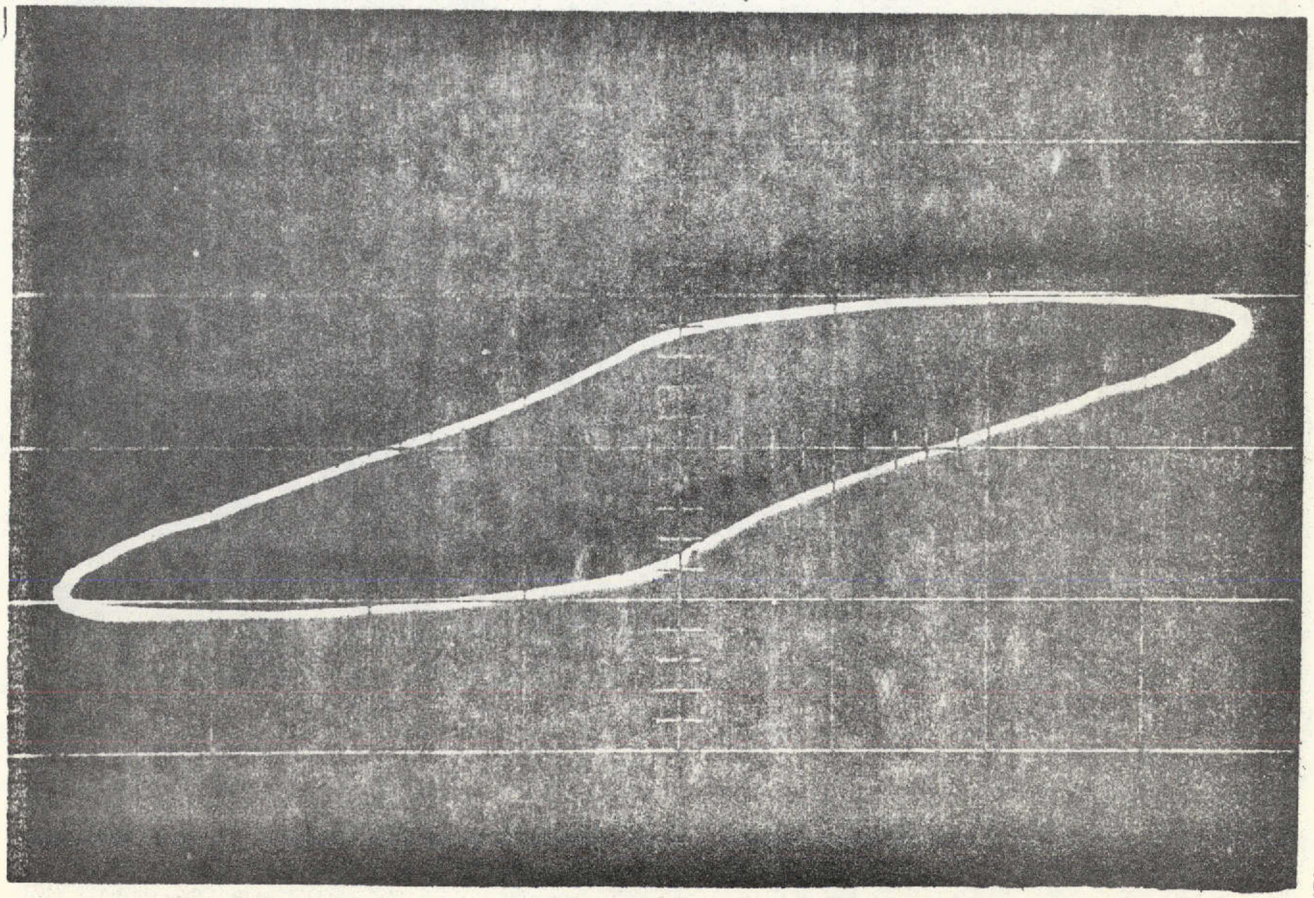
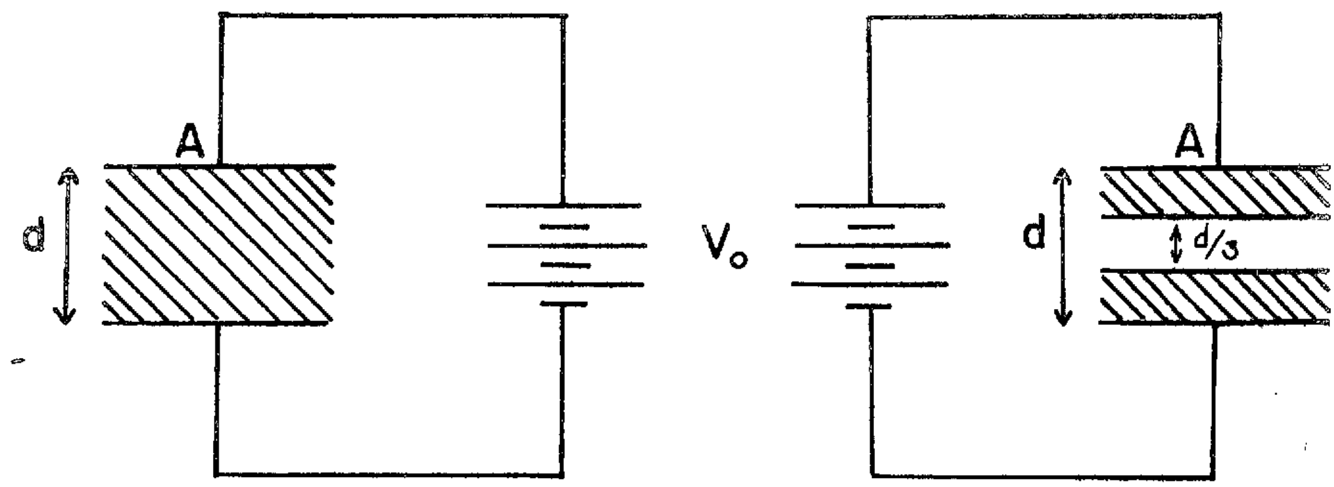


Figure 7.

Two identical capacitors, one completely filled with a dielectric and the other having a gap in the dielectric material.


A
d
V$_o$
d
A
d/3

In contrast, the electric field in the dielectric of the partially filled capacitor, whose dielectric constant is κ is given by

$$E_1 = \frac{V_o}{d}\left(\frac{3}{\kappa + 2}\right)$$

which is smaller than E_0 by a factor of $\left(\frac{3}{\kappa + 2}\right)$, or about 10^{-3} in the case of Rochelle salt. Suppose we have a large sample of Rochelle salt between two parallel capacitor plates. For a given applied voltage the region with more cavities experiences a lower average electric field and hence higher applied fields are needed to switch the polarization. In contrast, a region with less cavities would require relatively low voltage for switching. Consequently the S-value would appear low if the sample contains many cavities, even if the quality of the sample is excellent. (The hysteresis curve shown in the upper photograph in Fig. 6 was taken from a large good-quality earth-grown crystal.) The relatively low S-value is due to the large fringe effect which is inevitable for this preliminary experimental arrangement.

Thus it is important to develop a slicing technique capable of cutting this fragile crystal. Then it would be possible to examine the ferroelectric hysteresis of each sliced part in order to obtain accurate S-values.

II. Work Planned

1. Development of Slicing Technique

In our opinion none of the techniques that are currently available for slicing crystals are capable of cutting the fragile crystal returned from Skylab-4 without ruining it. Slicing the crystal is important for obtaining accurate S-values from hysteresis curves.

2. Observation of Ferroelectric Hysteresis and Domain Structure

The cavity concentration in the Skylab crystal differs from one region to another. Thus, we expect the ferroelectric quality will also differ from one region to another. For this reason, ferroelectric study of the sliced crystal is important.

3. Further Studies of Microscopic Cavities

A thinly sliced sample of the Skylab crystal should provide more detailed information about shape, structure, and distribution of microscopic defects present.

III. Expenditures

Man-hours expended through July 22, 1974 - 8 months

Cost Expenditures - $8,063

IV. Distribution

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Mr. Johnny M. Rogers Associate Director for Contracts & Grants Box 2846 University, Alabama 35486	1

V. References

1. See, for example, for review, D. T. J. Hurle, J. Cryst. Growth 13 (or 14), 39 (1972).
2. I. Miyagawa, Technical Summary Report, NASA Contract #NAS 8-28098, February 28, 1973.
3. I. Miyagawa, Technical Summary Report, NASA Contract #NAS 8-28098, May, 1974, p.38.