NUCLEATION OF CRYSTALS FROM SOLUTION IN MICROGRAVITY

(USML-1 GLOVEBOX (GBX) INVESTIGATION)

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ABSTRACT

A new method for initiating nucleation from solutions in microgravity which avoids nucleation on container walls and other surfaces is described. This method consists of injecting a small quantity of highly concentrated, heated solution into the interior of a lightly supersaturated, cooler host growth solution. It was tested successfully on USML-1, producing a large number of LAP crystals whose longest dimension averaged 1 mm.

BACKGROUND

There are two approaches to growing crystals from solution in microgravity; (1) seeded crystal growth, and (2) nucleated growth. In seeded crystal growth one starts with a high quality seed crystal, immerses it in a slightly supersaturated growth solution , and the seed crystal grows by the process of new growth layering on the seed. The growth rate is controlled by the degree of supersaturation of the growth solution; a low degree of supersaturation producing a low growth rate which is conducive to high crystal quality. A difficulty arises when evaluating the quality of the new growth area and relating it's quality to the microgravity processing environment. Defects and imperfections in the seed are often propagated into the new growth region. Ambiguities arise, therefore, when trying to interpret the characteristics of the new growth area because the effects of the seed may mask the effects of the growth environment.

In nucleated crystal growth, one produces a highly supersaturated solution in which over time spontaneous nucleation takes place and crystallites appear. The degree of supersaturation can be adjusted to provide optimum growth rates for the crystallites, which then grow to large size. Since these crystals were not grown from seeds their structural quality is not influenced by the quality of an underlying seed, and a relationship can be made between their quality and the microgravity processing conditions from which they were produced.

Another advantage of growing crystals from nucleated solutions is that it can offer a greater degree of flexibility compared to seeded growth. There are ways to control the number and size

distributions of crystals produced. Careful control of the nucleation process can produce anywhere from a very few to a great many crystallites. The growth of these crystallites into large single crystals can be controlled by adjusting the degree of supersaturation of the growth solution.

The favorable condition for nucleation is a high degree of supersaturation. The onset time for nucleation, along with the rate of nucleation, is governed by a curve which displays a very sharp increase in the nucleation rate over a narrow range of supersaturation. The favorable condition for the growth of crystallites into high quality large crystals is a low growth rate achieved by a low degree of supersaturation. Figure 1 shows the dependence of the nucleation rate, the growth rate and the mean crystal size on supersaturation.

A serious problem arises when nucleating in microgravity. The usual procedure used in a one-g environment is to cool the walls of a container of solution to drive the solution into supersaturation. Because of the absence of convection in microgravity, cooling the walls of the container only cools the adjacent solution leaving the interior solution to cool very slowly by conductive heat transport. Crystallites tend to nucleate first on the walls of the container, and do not form in the interior until a much later time when conductive heat transport has finally cooled the interior. As a result, control over the nucleation and growth rates will not be sufficient to produce the desired numbers of crystals of large size and high quality.

A new method for initiating nucleation from solutions in microgravity which avoids wall nucleation problems and adds considerable flexibility to the whole process has been developed by the authors.[2] This method consists of injecting a small quantity of highly concentrated, heated solution into the interior of a lightly supersaturated, cooler host growth solution. The injected solution, which is heated to above its saturation temperature, quickly cools in the presence of the cooler, lightly saturated host solution and forms a highly localized, highly supersaturated zone in which nucleation is soon initiated. Once crystallites form, they grow in the favorable concentration and temperature environment provided by the host solution. Considerable flexibility is offered by the combinations of injection solution and host solution temperatures and concentrations which can be chosen. It should be noted that because the rate of thermal diffusion is an order of magnitude greater than mass diffusion, the small globule of injected solution cools quickly and only slowly diffuses into the host solution, providing the needed time for the nucleation process to occur.

I. EXPERIMENT

The objective of this investigation, which was flown in the GBX facility onboard USML-1 launched on STS-50 from the Kennedy Space Center on June 25, 1992, was to demonstrate and evaluate the above described new technique for initiating and controlling the nucleation of crystals from

solution in a microgravity environment. Figure 3 shows the experiment apparatus. It consists of a fluid transfer unit (FTU), solution reservoirs, experiment cells, and a temperature probe and display. Aqueous solutions of L-Arginine Phosphate Monohydrate (LAP) , $C_6H_{14}N_4O_2$- H_3PO_4-H_2O, were used for both the nucleating and growth solutions. Three sequential runs were planned using nucleating solutions of LAP with concentrations of 42g, 38g, and 34g of LAP in 100g of H_2O. These were to be injected into growth cells filled with a host solution with a concentration of 18g LAP in 100g of H_2O. Figure 2 shows the solubility curve for LAP. At one end of each solution reservoir was an interior electric heater, a thermistor, a magnetic coupled stirrer, and a transfer port. At the other end was a piston used to drive the transfer of solution from the reservoir. On top of each reservoir was a electrical terminal for connection to the FTU controller. On top of each growth cell were ports for (1) filling with host solution, (2) injection of the nucleating solution, (3) a vent for exhausting air as the cell is filled, (4) a check valve with overfill chamber, and (5) a feed through for the temperature probe. The reservoirs containing the host solutions held a volume of 93 ml of which 70 ml were the maximum transferable. The reservoirs containing the nucleating solutions had an internal volume of 49 ml, however only about 0.99 ml of solution were injected for any given nucleation run. The growth cells had an internal volume of 67 ml. The FTU contained a Tattletale microprocessor programmed to control the heating, stirring, and transfer of solutions form the reservoirs. It also had a temperature display indicating the solution temperature in the reservoir being processed.

Mission constraints necessitated the stowage of the experiment solutions at ambient temperature (about 25·C) in their reservoirs for many weeks prior to launch. Because all of the concentrations used in the experiment are above saturation at room temperature, it was anticipated that crystallites would precipitate out of solution in the reservoirs during this stowage period, therefore the experiment was designed with the capability of heating and stirring the solution to dissolve the precipitated material.

II. PROCEDURE

The FTU was placed in the glovebox and connected to the glovebox power through two cables, one of which supplied 12 VDC for the electronics and the stirring motor and the other supplied 24 VDC for the heater and the stepper motor which pumped the solutions. A host solution reservoir was inserted into the FTU and the heater/thermistor cable was connected. The host solution was heated to 55·C and held at that temperature with stirring until all precipitated solute had dissolved. The solution was pumped through a flexible transfer tube and quick-disconnect fittings into the nucleation cell, which was then allowed to cool to glovebox ambient temperature (about 27·C). While the cell was cooling, the reservoir containing the nucleating solution was heated to 60·C and held at that temperature with stirring until the precipitated material was dissolved. When the cell reached ambient temperature, a Lexan injection tube

was connected to the injection reservoir, and hot solution was manually driven into the tube assembly by turning a knob on the FTU in order to purge all air from the assembly. The injection tube was then quickly inserted into the nucleation cell and a knob on the FTU was slowly turned to inject about 1 ml of the nucleating solution into the host solution. The solution transfer tube was then disconnected using the quick disconnect fitting, and the cell was bagged and attached to the laboratory module wall for periodic photography as nucleation occurred and the crystallites grew. The growth phase lasted for about 5 days.

III. Results

Nucleation did not occur in the first run because a number of large air bubbles were introduced into the host solution during experiment cell filling. These bubbles dispersed the nucleating solution in the host solution as it was injected, preventing the formation of the highly supersaturated region required for nucleation to occur. In the second run, the cell was filled more slowly by using the manual fill knob on the FTU instead of the filling motor. No bubbles were introduced in this case. The 34g LAP/100g H_2O nucleating solution was selected for this run, and it was successfully injected into the center of the cell, producing a nucleating region about 12 mm in diameter. Profuse nucleation occurred approximately 15 seconds after injection, producing a large number of crystallites. The crystallites eventually drifted to the wall of the cell opposite the end of the injection tube under the influence of residual gravity. Figure 3, taken during the flight, shows the cell with crystals. A few of them are still suspended near the center of the cell in the microgravity environment of the Spacelab module. The largest of the crystals grew to dimensions of about 3 x 5 x 0.5 mm. Most of the crystals were about 1 mm in their longest dimension. These were difficult to measure because they had clumped together after the flight and could not be separated without breakage. A total of 4.34g of crystals were recovered from the cell after it was returned to the laboratory. The third planned run could not be performed because of time constraints.

CONCLUSION

This experiment successfully demonstrated the value of our new method of initiating nucleation in a solution in microgravity in providing significantly better control over nucleation and growth processes than conventional techniques. A predetermined volume of nucleating solution was deployed in the desired location in a growth solution-filled cell. Nucleation was restricted to this well defined region near the center of the cell, and crystallites were grown. The nucleation onset time was much shorter than expected based on the results of ground control experiments using the same concentrations. In these experiments a series of solutions of various concentrations were prepared and loaded into test tubes which were then sealed and allowed to cool to room temperature. These tubes were inspected periodically, and the time of the appearance of visible nucleation was noted. The reason for the

difference between ground-based and flight onset times has not yet been determined, but turbulence in the nucleating solution during injection, and the high cooling rate may have been important factors. Further experiments will emphasize the optimization of the solution concentrations to improve control of the nucleation rate. With finer control over nucleation, this method will permit more precise control over growth parameters which control crystal characteristics.

REFERENCES

1. J. Nyvlt, O. Sohnel, M. Matuchova and M. Kroul, *The Kinetics of Industrial Crystallization,* Elsevier, NY, p35

2. U. S. Patent No. 5,173,087, Crystal Growth in a Microgravity Environment, December 22, 1992

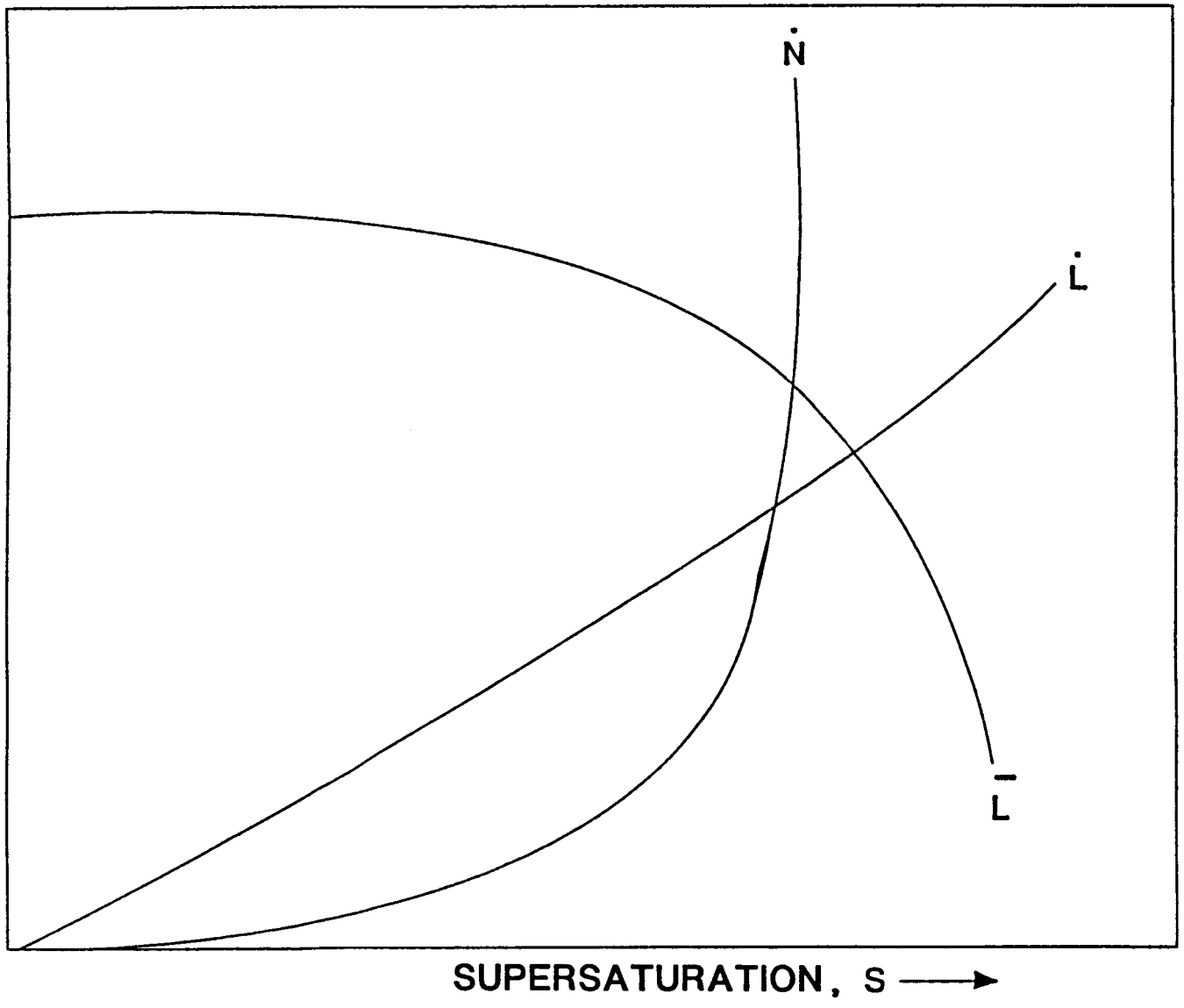

Figure 1 Dependence of the nucleation rate ($\dot{N}$), the crystal growth rate ($\dot{L}$), and the mean crystal size ($\bar{L}$) on the supersaturation (S).[1]

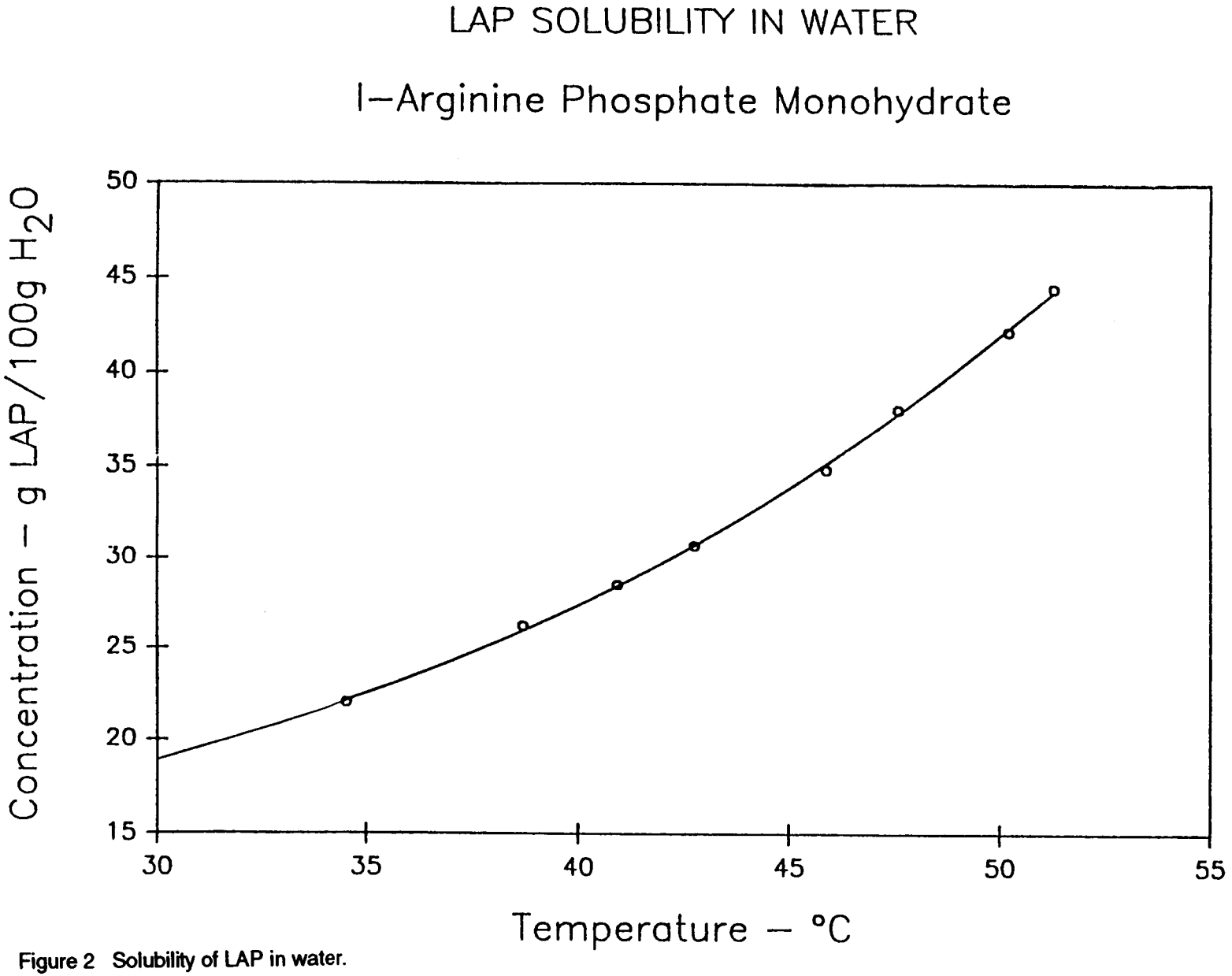

Figure 2 Solubility of LAP in water.

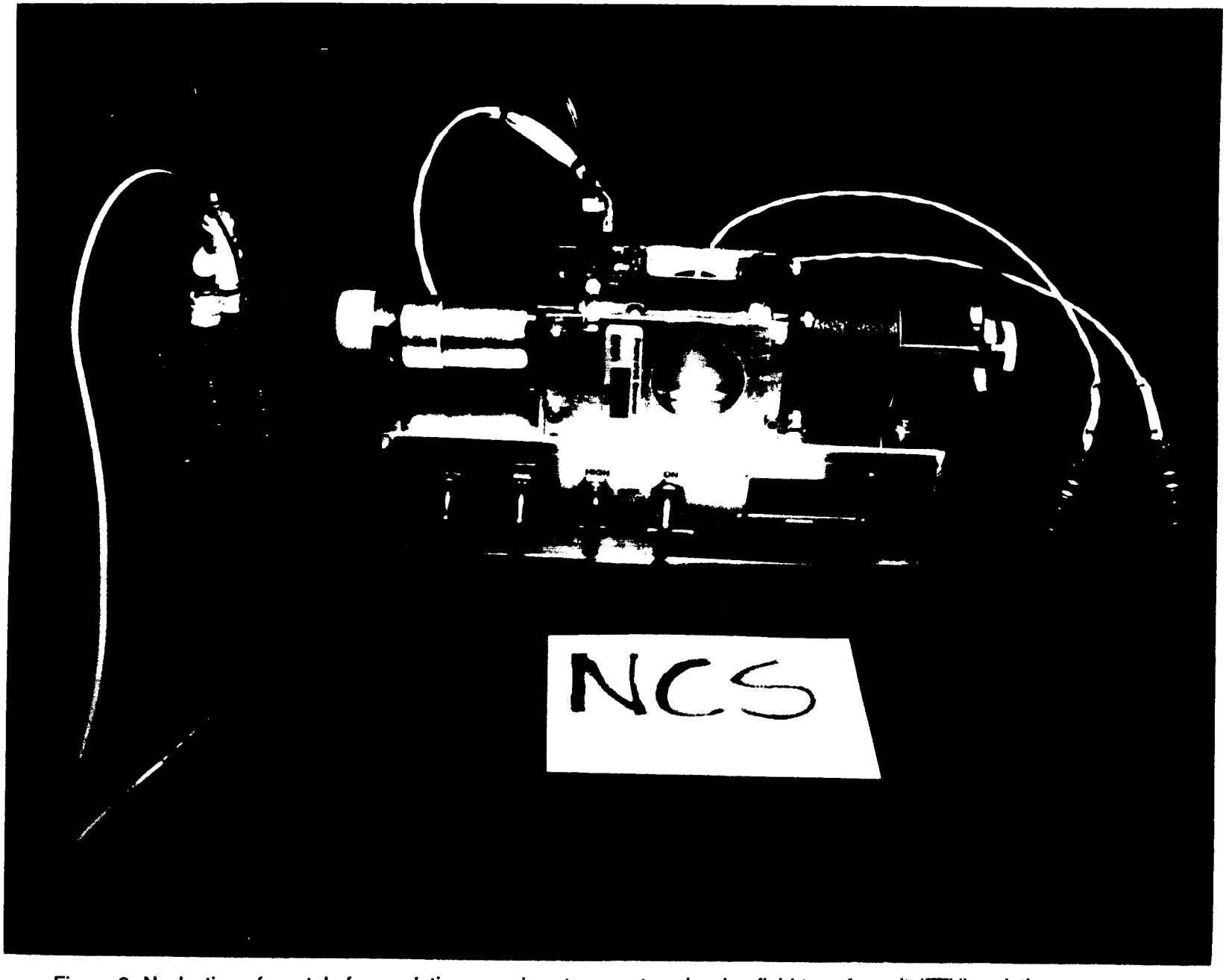

Figure 3 Nucleation of crystals from solution experiment apparatus showing fluid transfer unit (FTU), solution reservoir (mounted in FTU), experiment cell, and temperature display.

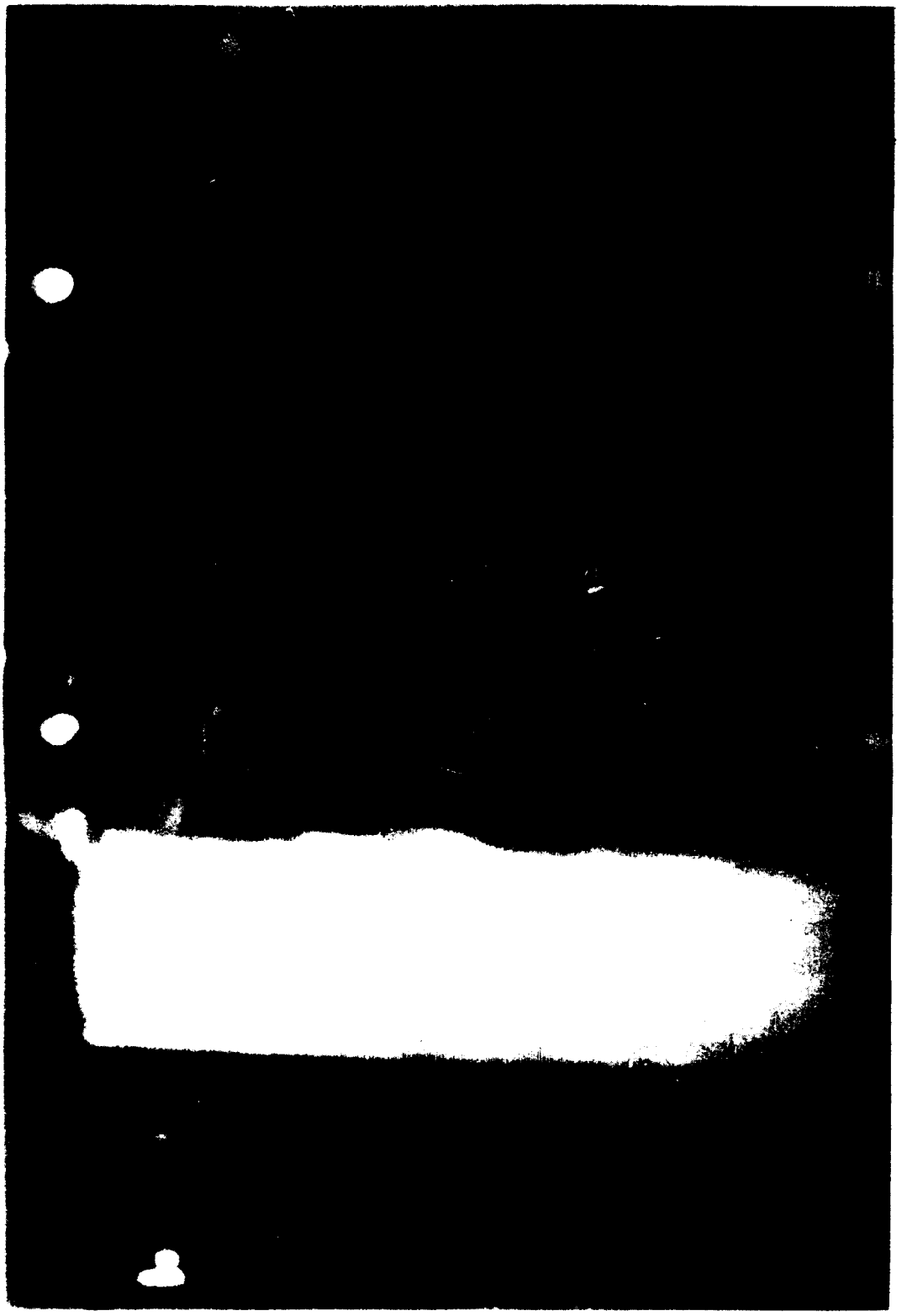

Figure 4 Experiment cell containing growing crystals, taken during flight of USML-1.

Discussion
(Speaker: Donald Reiss, NASA MSFC)

Question: *Did you do anything to agitate the solution to make sure there was not basically a local heavier concentration because as you were trying to dissolve the crystals, the nutrient had to diffuse into the solute ?*

Answer: Are you talking about the reservoir before we injected it ?

Question: *Yes*

Answer: Yes. Again, because we had problems with the stirrer, we did have Carl manually agitate the apparatus repeatedly. I think it was every 10 minutes, or so, until he could see that certainly there was no solid material in there; but, we tried to get as good mixing as we could under the circumstances.

Question: *Could you comment on what the possibility was of getting pre-embryonic or embryonic sizes while it was coming down the tube ?*

Answer: That is certainly a possibility if you get some substantial cooling in there. We had no way of measuring it. The way we tried to avoid it was just to heat the solution well enough above equilibrium. That and, then of course, the tubing itself is an insulated material, so we were hoping that if we worked quickly enough that we wouldn't have time to cool into supersaturation before that injection took place. The equilibrium temperature was 45 and we heated to 60. We are just assuming that we are reasonably under-saturated before we did the injection. I didn't see in the video any salt particles coming out of the tube. It looked clean.

Question: *Did you purge the tube ?*

Answer: Yes, we did purge the tube.

Question: *But critical nuclei sizes are below what you could see ?*

Answer: Yes, you wouldn't be able to see it.