

Crystal Growth from Solutions in Low Gravity

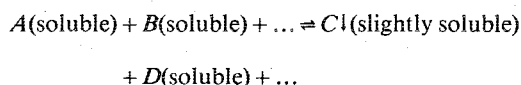
M. D. Lind*

Rockwell International, Thousand Oaks, Calif.

An experiment performed during the Apollo-Soyuz flight investigated a novel process for growing single crystals from solutions. In zero gravity, reactant solutions were allowed to diffuse slowly toward each other through a region of pure solvent in which they underwent a chemical reaction to form crystals of an insoluble material. The process is analogous to the growth of crystals in gels in normal gravity. The experiment was successful and yielded crystals of about the expected size, number, and quality. The results indicate that with further refinement the process should yield large, high-quality crystals of a variety of materials.

I. Introduction

SINGLE crystals of slightly soluble substances often can be grown by using a gel to separate two or more reactant solutions and thus allowing them to diffuse together slowly and react according to a chemical equation of the following type as the crystal grows:



Typical experimental arrangements for gel methods of crystal growth are shown schematically in Fig. 1. In the *u*-tube arrangement (Fig. 1a) the crystals normally grow within the gel or at the interfaces with the reactant solutions. In the second arrangement (Fig. 1b) the crystals can grow in the pure solvent at the center. In these processes, the primary functions of the gel are 1) suppression of rapid convective mixing caused by differences in the densities of the reactant solutions and 2) support of the growing crystal. Diffusion is the predominant mechanism for the mixing of the reactant solutions. This permits control of the material transport by variation of concentrations and/or reactor geometry. Typical gels are approximately 95% solvent by weight. As the crystals grow, they are exposed to the solution on all sides and have no contact with container surfaces except those of the flexible gel structure.

It was hypothesized that in an environment of sufficiently low gravity, convection and sedimentation become negligible. Then the gel is not needed for suppressing these processes and can be replaced by a region of pure solvent. Diffusion should be the predominant mixing mechanism even with no gel present. Experiments to test this hypothesis were performed in space during the recent Apollo-Soyuz Test Project (ASTP).

Gel methods of crystal growth, like most aqueous solution growth methods, are advantageous because crystal growth occurs at ambient ($\sim 25^\circ\text{C}$) temperature. This minimizes problems of thermally or mechanically induced strain, phase transformations, volatility of components, contamination by the container, etc., often inherent in high-temperature growth methods. However, gel methods also have certain disadvantages, including excessive nucleation resulting in small crystal sizes, contamination of the crystals by gel constituents or impurities in the gel, and gel instability. The space flight experiments may be expected to overcome all these disadvantages while retaining the advantages.

Presented as Paper 77-197 at the AIAA 15th Aerospace Sciences Meeting, Los Angeles, Calif., Jan. 24-26, 1977; submitted Feb. 18, 1977; revision received Nov. 8, 1977. Copyright © American Institute of Aeronautics and Astronautics, Inc., 1977. All rights reserved.

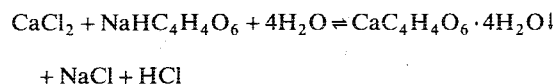
Index category: Space Processing.

*Member of Technical Staff, Science Center.

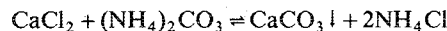
II. Experimental Procedure

The nature of the experiments and the choice of reactions to be investigated were strongly influenced by the short duration of the flight. To simplify the experimental apparatus, the usual requirement for precise temperature control was eliminated by choosing crystals that can be grown at ambient temperature without precise temperature control. Three reactions were investigated:

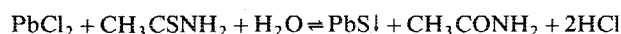
Calcium tartrate:



Calcium carbonate:



Lead sulfide:



These were chosen for the following reasons:

- 1) They are easily grown in gel systems and the methods have been well studied so that growth conditions were known and results were readily available for comparison with ASTP results.
- 2) Calcium tartrate is an especially important model material for investigation of gel growth mechanisms.
- 3) Calcium carbonate is a typical example of crystals that

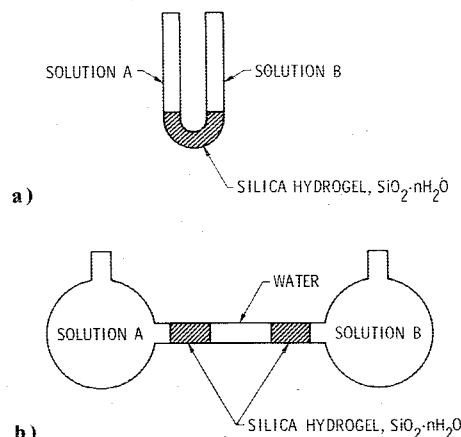


Fig. 1 Typical experimental arrangements for gel methods of crystal growth.

are contaminated by gel constituents and therefore can be improved by growth without the gel.

4) Calcium carbonate and lead sulfide have technological importance.

The experimental conditions for the ASTP experiments were based on results of previous gel growth and other experiments.¹⁻¹² It was assumed that the diffusion and crystal growth processes would not be very different if the gel was replaced by a region of pure solvent, and this assumption appears to have been validated by the ASTP results. The important experimental parameters are selection and concentrations of reactant solutions, reactor dimensions, and hydrogen-ion concentration (pH) of the growth medium (water). The values of these parameters used in the ASTP experiments are summarized in Table 1.

The apparatus consisted of six specially designed and fabricated reactors (Fig. 2). Each reactor had three compartments that were separated by valves operated by the knobs at each end. Each compartment had a separate filling port. The compartments varied in length, as indicated in Table 1. The reactors were constructed of Lexan polycarbonate resin. Their covers were flat and transparent to permit photographing the progress of diffusion and crystal growth.

Before delivery of the hardware to the launch facility, the reactors (with the intercompartment valves in the closed positions) were filled with the various solutions. The reactant solutions were placed in the outer compartments of each reactor, and the central compartment was filled with water.

The six reactors were mounted in the U-4 locker in the Apollo command module. They were accessible in this location, yet out of the way of other operations. After the joint phase of the flight, at approximately 109 h ground elapsed time (GET), a crewman activated the experiments by opening the intercompartment valves to allow the reactants to begin diffusing toward the center. At the time of activation and at approximately 12-h intervals for the remainder (116 h) of the flight, a crewman took photographs of the six reactors.

III. Results

Crystals of about the expected size, quality, and number formed in all six reactors. Experiment results are shown in

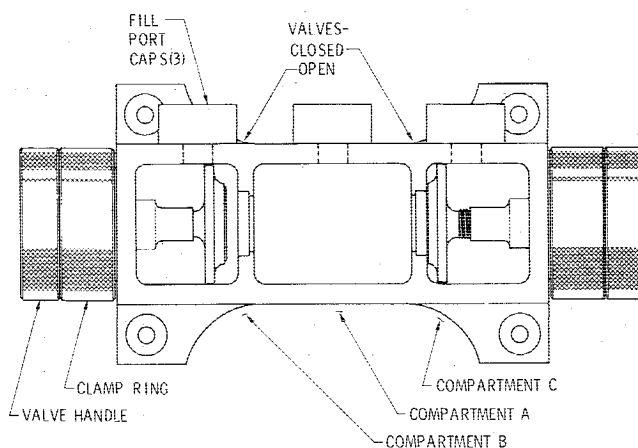


Fig. 2 Schematic diagram of a reactor.

Figs. 3-5, which are photographs taken after return of the reactors to the laboratory. Upon receipt of the reactors and before opening them, the reactors and their contents were examined visually through the reactor faces with a binocular polarizing microscope of 40× magnification. The reactors were photographed with 1.5× magnification, and representative crystals were photographed through the reactor faces with 10× magnification. Following this procedure, representative crystals were removed through the center fill ports for further examination. The identity of each kind of crystal was confirmed by single crystal x-ray diffraction data obtained with Buerger precession and Gandolfi cameras. As expected, the x-ray diffraction data are identical with those of Earth-grown crystals.

The best crystals obtained were the calcium tartrate crystals (Fig. 3). This result was not surprising because these crystals are among the easiest to grow by gel methods. Both calcium tartrate reactors produced numerous prismatic crystals with maximum dimensions as large as 2 mm and platelike crystals as long as 5 mm; these crystals have good face development, are very clear, and appear free of strains when viewed in the microscope with light transmitted through crossed polarizers.

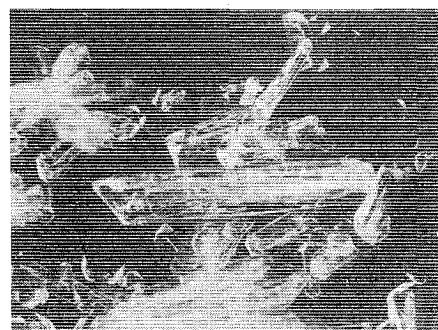
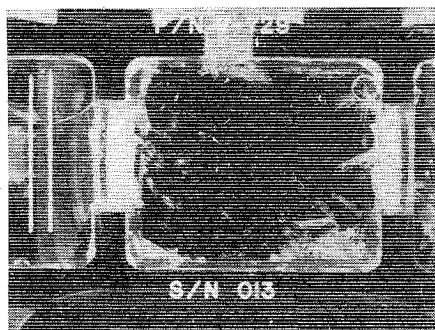
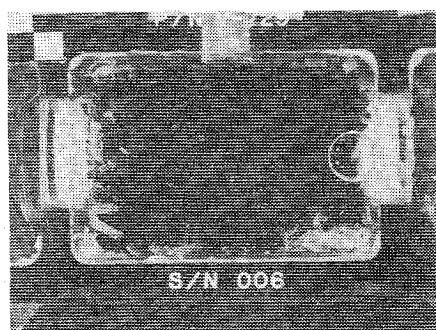


Fig. 3 Calcium tartrate.

Table 1 Reactant solutions

Reactor serial number	Compartment B		Compartment A		Compartment C	
	Reactant	Length, cm	Reactant	Length, cm	Reactant	Length, cm
005	0.1M CH ₃ CSNH ₂	3.30	H ₂ O adjusted to pH=1.0 with HCl	5.08	Saturated PbCl ₂	3.30
006	0.5M CaCl ₂	3.30	H ₂ O	5.08	0.45M NaHC ₄ H ₄ O ₆	3.30
007	0.5M CaCl ₂	3.30	H ₂ O	5.08	0.5 M (NH ₄) ₂ CO ₃	3.30
008	0.1 M CH ₃ CSNH ₂	3.30	H ₂ O adjusted to pH=0.5 with HCl	5.08	Saturated PbCl ₂	3.30
012	0.5M CaCl ₂	4.19	H ₂ O	4.19	0.5 M (NH ₄) ₂ CO ₃	3.30
013	0.5M CaCl ₂	4.19	H ₂ O	4.19	0.45M NaHC ₄ H ₄ O ₆	3.30

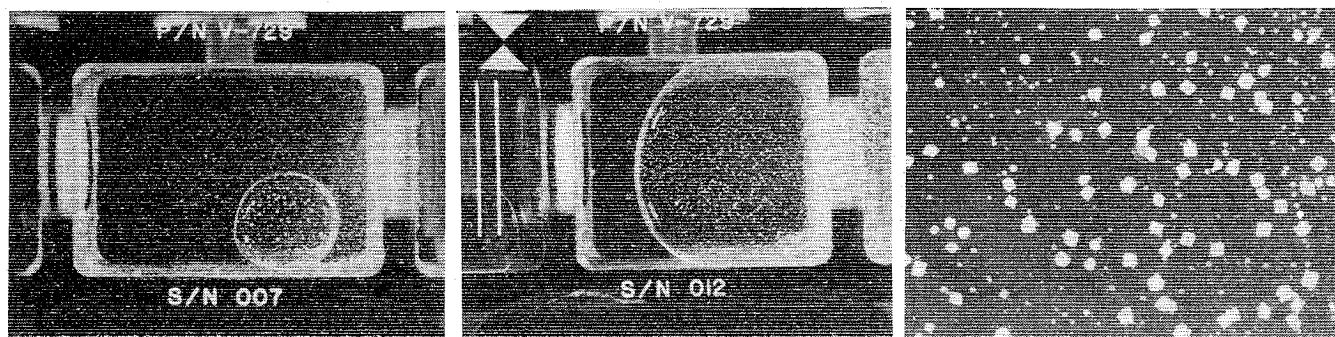


Fig. 4 Calcium carbonate.

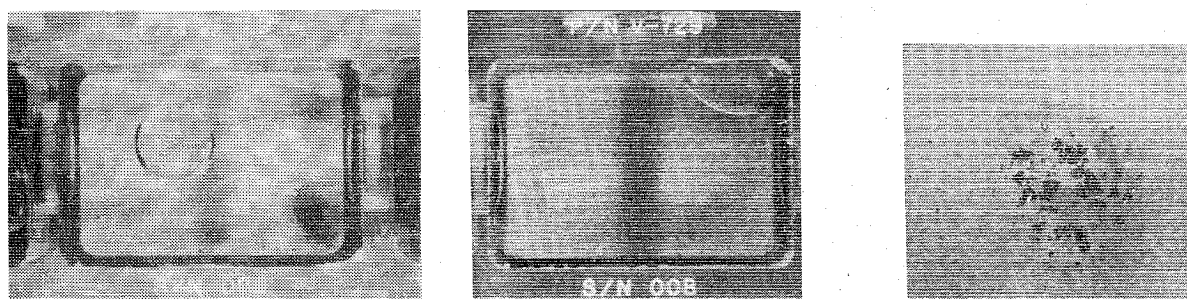


Fig. 5 Lead sulfide.

For several calcium tartrate crystals, x-ray diffraction topographs were obtained with a Lang camera for comparison with those of Earth-grown crystals. To date, these comparisons indicate about equal crystal quality. There were also a few platelike crystals as long as 10 mm, but of somewhat poorer quality. The absence of finely divided precipitate indicated that mixing of the reactant solutions and crystal growth were complete by the time of spacecraft reentry, which was the desired result. Contrary to the experience with gel experiments, the platelike crystals were more numerous and larger than the prismatic crystals. Platelike crystals have been obtained occasionally in gel experiments, but the prismatic habit is more usual. The reasons for this variation in habit and its significance are unknown at this time.

Each of the two calcium carbonate reactors produced numerous well-formed clear rhombohedral crystals as long as 0.5 mm on an edge (Fig. 4). These crystals are very similar in appearance to Earth-grown calcium carbonate crystals, both synthetic and natural. Although small, they are large enough to exhibit birefringence. Again, no finely divided precipitate resulted, which indicates that, as desired, mixing of the reactant solutions and crystal growth were complete by the time of spacecraft reentry. Most of the calcium carbonate crystals adhered to the reactor, which implies that for CaCO_3 growth the polycarbonate material is not the best surface for the interior walls of the reactors.

The two lead sulfide experiments were less successful, but both resulted in the production of discrete single crystals with dimensions as large as 0.1 mm (Fig. 5). In this case, the mixing and reaction were not complete at the time of reentry. A fine precipitate was observed that continued to increase even after return of the reactors to the laboratory. This result indicates that a longer time is needed for successful growth of larger lead sulfide crystals under the conditions used. An alternative way of obtaining better results is to use a somewhat higher temperature to increase the solubility of one of the reactants (lead chloride).

The calcium carbonate crystals are easily visible in the series of photographs taken at 170 h GET (6 h after activation of the experiment) and are increasingly visible in subsequent

photographs. Representative photographs are shown in Fig. 6. A small number of calcium tartrate crystals also appear in these photographs, but less clearly. The photographs indicate that most of the calcium tartrate crystals must have grown after the last series of photographs was taken. The flight continued for more than 6 h after the last series of photographs; therefore, it is quite possible that substantial growth occurred after that time. It is very likely that the calcium tartrate crystal growth was complete before reentry, because virtually all the calcium tartrate crystals were free of the reactor walls as if they were grown in low gravity. Repeated experiments have shown that rapid mixing in normal gravity will result in a much smaller particle size and that the crystals thus formed adhere to the bottom of the reactor. It is reasonable to assume that reactant concentrations were just reaching the values required for calcium tartrate growth at the end of the flight. It was also observed that some additional calcium carbonate crystals grew after the last series of photographs was taken.

The photographs also provide a record of the movement of air bubbles in the reactors during the flight. The air bubbles migrated from the expansion spaces in the fill-port caps during handling of the reactors before flight. It would have been preferable to avoid the presence of the bubbles, but they apparently did not have any significant negative effect on the experiments. In fact, their presence allowed the beneficial effect of a rough evaluation of the accelerations experienced by the reactors. It is interesting to observe that air bubbles in the two calcium tartrate reactors remained stationary throughout the flight. Bubbles in the calcium carbonate and lead sulfide reactors were more mobile but remained stationary for as long as the 12-h interval between photographs. The difference in mobility of bubbles in the various reactors is not yet understood; however, movement of the bubbles shows that accelerations experienced by the reactors during the flight were small.

During the flight, the cabin temperature ranged between approximately 24°C (75°F) and approximately 16°C (60°F). Such large temperature variations were not expected when the decision was made to neglect temperature control to simplify the experimental hardware. Solubilities of the reactants and

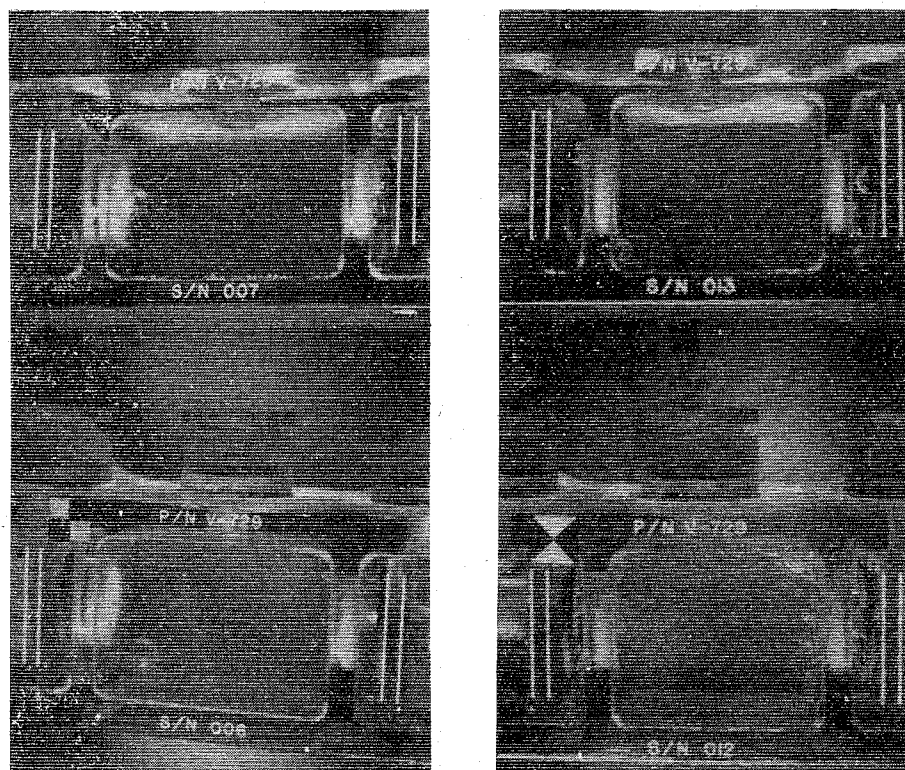


Fig. 6a 170 h GET.

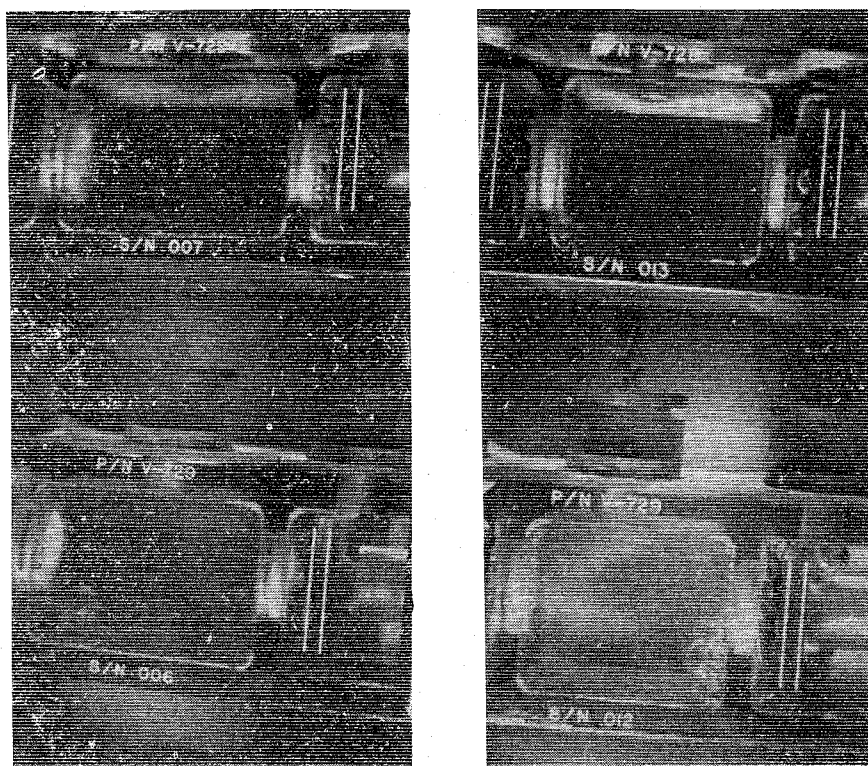


Fig. 6b 218 h GET.

crystalline products are strongly dependent on temperature, and the temperature variations were sufficient to markedly affect the results of the experiments. Nucleation was excessive in all six reactors, which indicates the need for considerable refinement of the experimental parameters to suppress nucleation and improve crystal size and quality. Precise

temperature control is probably one of the most important improvements to be made.

The results proved the feasibility of this novel method of crystal growth and indicate that the method, with further refinement, should yield superior crystals of a variety of materials. It appears likely that conditions can be optimized

to produce larger crystals than can be obtained with gels. High purity remains a major potential advantage of this method.

Acknowledgment

Partially supported by NASA Contract NAS9-14015. The author thanks J. R. Bates, A. G. Mitchell, R. M. Housley, A. H. Muir, and W. M. Robertson for helpful discussions of the experiments. He thanks C. J. Le Blanc, L. K. Redmond, N. G. Taylor, G. E. Garing, and D. D. Matthews for their important contributions to the design and performance of the experiments, and T. P. Stafford, D. K. Slayton, and V. D. Brand for performing the experiments during the Apollo-Soyuz flight.

References

- ¹Henisch, H. K., *Crystal Growth in Gels*, Pennsylvania State University Press, 1970.
- ²Henisch, H. K., Dennis, J., and Hanoka, J. I., "Crystal Growth in Gels," *Journal of Physics and Chemistry of Solids*, Vol. 26, March 1965, pp. 493-500.
- ³Nickl, H. J. and Henisch, H. K., "Growth of Calcite Crystals in Gels," *Journal of the Electrochemical Society*, Vol. 116, Sept. 1969, pp. 1258-1260.
- ⁴Barta, C., Zemlicka, J., and Rene, V., "Growth of Calcium Carbonate and Calcium Sulfate Dihydrate Crystals in Gels," *Journal of Crystal Growth*, Vol. 10, Aug. 1971, pp. 158-162.
- ⁵Blank, Z. and Brenner, W., "The Growth of Group II-VI Crystals in Gels," *Journal of Crystal Growth*, Vol. 11, Dec. 1971, pp. 255-259.
- ⁶Blank, Z. and Brenner, W., "Research Directed Toward Preparation of Compound Semiconductors by Controlled Diffusion Mechanism in Gels," AFCRL-70-0252, Air Force Cambridge Research Labs., L. G. Hanscom Field, Mass., March 1970.
- ⁷Blank, Z., Brenner, W., and Okamoto, Y., "The Growth of Lead Sulfide in Silica Gels at Ambient Temperatures—Preliminary Characterization and Effect of Various Organic Compounds as Sulfide Ion Donors," *Material Research Bulletin*, Vol. 3, July 1968, pp. 555-561.
- ⁸Swift, E. H. and Butler, E. A., "Precipitation of Sulfides from Homogeneous Solutions by Thioacetamide," *Analytical Chemistry*, Vol. 28, Feb. 1956, pp. 146-153.
- ⁹Armington, A. F., DiPietro, M. A., and O'Connor, J. J., "A Study of Some Factors which Influence the Growth of Cuprous Chloride in Silica Gel," AFCRL-67-0445, Air Force Cambridge Research Labs., L. G. Hanscom Field, Mass., July 1967.
- ¹⁰Armington, A. F. and O'Connor, J. J., "Some Factors Influencing the Growth of Crystals in Gel by the Complex Dilution Method," *Material Research Bulletin*, Vol. 3, Dec. 1968, pp. 923-931.
- ¹¹Kirov, G. K., "On the Diffusion Method for Growing Crystals," *Journal of Crystal Growth*, Vol. 15, Aug. 1972, pp. 102-106.
- ¹²Torgesen, J. L. and Peiser, H. S., "Method and Apparatus for Growing Single Crystals of Slightly Soluble Substances," U.S. Patent 3,371,036, Feb. 27, 1968.

From the AIAA Progress in Astronautics and Aeronautics Series . . .

SPACE-BASED MANUFACTURING FROM NONTERRESTRIAL MATERIALS-v. 57

Editor: Gerard K. O'Neill; Assistant Editor: Brian O'Leary

Ever since the birth of the space age a short two decades ago, one bold concept after another has emerged, reached full development, and gone into practical application—earth satellites for communications, manned rocket voyages to the moon, exploration rockets launched to the far reaches of the solar system, and soon, the Space Shuttle, the key element of a routine space transportation system that will make near-earth space a familiar domain for man's many projects. It seems now that mankind may be ready for another bold concept, the establishment of permanent inhabited space colonies held in position by the forces of the earth, moon, and sun. Some of the most important engineering problems are dealt with in this book in a series of papers derived from a NASA-sponsored study organized by Prof. Gerard K. O'Neill: how to gather material resources from the nearby moon or even from nearby asteroids, how to convert the materials chemically and physically to useful forms, how to construct such gigantic space structures, and necessarily, how to plan and finance so vast a program. It will surely require much more study and much more detailed engineering analysis before the full potential of the idea of permanent space colonies, including space-based manufacturing facilities, can be assessed. This book constitutes a pioneer foray into the subject and should be valuable to those who wish to participate in the serious examination of the proposal.

192 pp., 6 × 9, illus., \$15.00 Mem., \$23.00 List

TO ORDER WRITE: Publications Dept., AIAA, 1290 Avenue of the Americas, New York, N. Y. 10019