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ELECTROCHEMICAL DEPOSITION OF SILVER CRYSTALS ABOARD SKYLAB IV

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16. Abstract

Silver crystals were grown aboard Skylab IV by an electro-chemical reaction and subsequently returned to earth for comparison with crystals grown at 1- and 5-g. Both the Skylab and earth-grown crystals show a variety of structures. Certain tendencies in structure dependency on gravity level, however, can be discerned. In addition, downward growing dendrite streamers; upward growing chunky crystal streamers; growth along an air/liquid interface; and ribbon, film, and fiber crystal habits were observed in experiments conducted on the ground with solutions of varying concentrations. It was also observed that the crystal structures of space and ground electro-deposited silver crystals were very similar to the structures of germanium selenide and germanium telluride crystals grown in space and on the ground by a vapor transport technique.

Consideration of the data leads to the conclusions that:

- The rate of electrochemical displacement of silver ions from a 5 percent aqueous solution by copper is predominantly diffusion controlled in space and kinetically controlled in 1- and higher-g because of augmentation of mass transport by convection.
- Downward and upward crystal streamers are the result of gravity-driven convection, the flow patterns of which can be delineated. Lateral growths along an air/liquid interface are the result of surface-tension-driven convection, the pattern of which also can be delineated.
- Electrolysis in space or low-g environments can produce either dendritic crystals with more perfect microcrystalline structures or massive, single crystals with fewer defects than those grown on ground or at higher g-levels. Ribbons or films of space-grown silicon crystals would find a ready market for electronic substrate and photocell applications. Space-grown dendritic, metal crystals present the possibility of unique catalysts. Large perfect crystals of various materials are desired for a number of electronic and optical applications.
- Vapor transport growth of germanium selenide and germanium telluride is affected by convection mechanisms similar to the mechanisms hypothesized for the electrochemical deposition of silver crystals.

Evidence and considerations leading to the preceding summaries and conclusions are presented. The implications of the findings and conclusions for technological applications are discussed, and recommendations for further experiments are presented.

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INTRODUCTION

During the Skylab IV mission a number of science demonstration experiments were conducted aboard the spacecraft. The opportunity for conducting these experiments arose when it became apparent that the astronauts were becoming so efficient in performing their primary duties that they would have some extra time for additional experiments. The science demonstration experiments were very simple in nature and operation because severe constraints were imposed by primary mission objectives. Some of the constraints included weight and volume limits, zero power, safety considerations, equipment compatible with spacecraft systems and operations, and limited astronaut training. Because of these constraints, the purpose of the experiments was primarily demonstration. Being, however, among the relatively few experiments in materials science that have been performed thus far in space environments, the demonstration experiments have provided useful and, in a number of cases, unexpected data as well as striking visual demonstrations of various physical phenomena in low-g [1].

The science demonstration reported herein was called TV106 – Deposition of Silver Crystals. It was performed on January 24, 1974, by Astronaut G. Carr. The purpose of this experiment was to demonstrate crystal growth by electrochemical reaction in low-g (1-g equals gravity acceleration at earth surface, or 980 cm/s^2) and to compare the resultant crystals with those grown on earth. The experiment consisted of inserting a scored, insulated copper wire into a 5 percent (by weight) aqueous solution of silver nitrate and allowing the crystal growth to proceed for the remainder of the mission. Silver crystals deposit when a copper wire is placed in a silver nitrate solution as indicated by the following overall electrochemical reaction:

$$Cu + 2\,Ag^{+} \rightarrow Cu^{++} + 2\,Ag$$

i.e., copper displaces silver ions from solution. The standard electrochemical potential calculated for the reaction is +0.4536 V. The electrochemical process can be viewed as an electrolysis in which the copper wire serves as an anode and deposited silver as the cathode as shown in Figure 1.

Commander Carr photographed the crystal growth after 6, 24, and 76 hours; but, unfortunately, no pictures developed on the exposed film. The crystals immersed in spent solution, however, were returned to earth for examination. Figure 2 shows the crystals (center tube) as received. The two side vials show crystals grown on earth for the same length of time as the flight crystals. It is apparent that jars during handling and re-entry dislodged the flight crystals from their growth sites. The returned flight crystals and crystals grown under a variety of conditions on earth, including gravity levels of 2- and 5-g, were examined by scanning electron microscope. Further details of the experiments are given in Appendix A. Both the Skylab and earth-grown crystals show a variety of structures. Certain tendencies in structure dependency on gravity level, however, can be discerned. The differences between the low-g and higher-g crystals are summarized as follows:

- The low-g crystals are more powdery or less coherent than the higher-g crystals. Furthermore, the higher the g-level, the more coherent the crystals.
- The low-g crystals show smaller, more perfect crystalline forms than do the higher-g crystals. Also, the higher the g-level, the more imperfect the resultant structures.
- The higher-g crystals show evidence of rapid growth from edges and corners.
- The 1-g crystals show examples of curvatures caused by fluid flow which are not observed in the low-g crystals.
- Steps and ledges appear more prevalent in the higher-g crystals than in the low-g crystals.
- Twinning appears more prevalent as gravity level increases.

Ground and centrifuge tests have yielded additional relevant information which is summarized as follows:

- After a number of hours, dilute solutions develop dendrite streamers that grow downward, i.e., in the same direction as the gravity vector. Concentrated solutions produce streamers of chunky, imperfect crystals that grow upward, i.e., in a direction opposite of the gravity vector.
- Centrifuging low concentration solutions increases coherency and size of the dendrite streamer.
- Crystal streamers in high concentration solutions spread out over a free liquid-gas surface when they encounter the same.
- More gas is apparently generated as concentration or gravity level increases.

The data are explained as follows: In the absence of natural convection (i.e., the low-g case), crystal growth rates are diffusion controlled, resulting in more dendritic deposits. The presence of convection throws the crystal growth rates into the kinetically controlled regime, resulting in larger, more compact crystals and upward growing streamers.

In the following sections, evidence and considerations leading to the preceding summaries and conclusions are presented. In addition the similarities between low-g electrodeposition and low-g vapor deposition are discussed. Observations of electrodeposition of metallic films, ribbons, and fibers are reported, and the possibility of growing films or ribbons of germanium and silicon is discussed. The implications for technological applications of the findings reported herein are discussed, and recommendations for further experiments are presented.

CRYSTAL COHERENCY AS FUNCTION OF G-LEVEL OR CONVECTION

One of the most obvious differences between the variously grown crystals is increasing coherence as gravity level increases. The flight crystals were a loose, coarse powder when received. Crystals grown at 1-, 2-, and 5-g, however, show increasing coherency. Such dependency of coherency on g-level is readily explained in terms of convection. For illustrative purposes, consider the depositing of silver ions on a silver electrode as shown in Figure 3; transport of silver ions to the silver cathode surface is determined by the indicated transport mechanisms. At the electrode surface, discharge of silver ions occurs by a series of steps but is indicated as a single step whose rate is determined by a rate constant k. It is obvious that the slowest of the noted sequential rate processes will determine the overall rate of silver deposition. If the rate of ion transport to the electrode surface is slower than the rate of electrochemical reaction, the process will be transport controlled. If, however, the rate of electrochemical deposition is the slowest of the various rate processes, the process will be kinetically controlled.

The same types of considerations apply to the anodic dissolution of copper. The cumulative effect of the various rates involved in the anodic and cathodic processes determines the ultimate nature of the silver deposit. Because dissolution of copper would not be expected to involve a high activation energy (i.e., a high anodic overpotential), the overall rates of electrochemical deposition can be assumed to be controlled by the deposition rates.

As indicated previously, deposition of silver ions onto a silver crystal attached to a copper wire may be viewed as an internal electrolysis in which deposited silver is the cathode and the copper wire is the anode. If it were possible to obtain current-versus-potential data for such a system, the plot would appear somewhat as shown in Figure 4. As indicated, at high potentials or high driving forces, the deposition rate is essentially transport controlled. As soon as a silver ion reaches the electrode surface, it is deposited. At lower potentials or driving forces, the rate of electrochemical reaction determines the overall rate. The deposition in this region or regime is kinetically controlled.

It is fairly well established that transport-controlled crystal growth tends to yield dendrites, while kinetic-controlled crystal growth yields faceted crystals. Also, the rate of nucleation increases with decreasing concentration [2] (see Sections 3 and 4 for further discussion). In a diffusion-controlled deposition in which the nucleation rate is uncontrolled, numerous small dendrites with many projections which can be easily knocked off generally result, and a more powdery deposit can generally be expected than in the case of kinetically controlled deposits. Thus, it is observed [2] that electrolytically deposited metal powders are produced in the transport-controlled regime of the current-potential curve and coherent deposits in the kinetically controlled regime. In the absence of gravity, the transport mechanism of gravity-driven convection is lacking. As a result, the total rate of ion transport is decreased in low-g environments (or, equivalently, the diffusion boundary layer is increased), and the crystal growth rate tends to be transport controlled, resulting in more dendritic deposits. On earth, vigorous buoyancy convection tends to make the process kinetically controlled. The reason for the more powdery nature of the flight crystals, therefore, is readily explained.

CRYSTALLINE STRUCTURE AS A FUNCTION OF G LEVEL OR CONVECTION

The Skylab and earth-grown crystals show a variety of structures. From a rather large number of scanning electromicrographs, however, certain tendencies in structure dependency on gravity level can be discerned. The noted differences consist basically of the following:

- The low-g crystals show smaller, more perfect crystalline forms than do the higher-g crystals.
- The higher the gravity level, the more imperfect the resultant structure.
- The higher-g crystals show evidence of rapid growth from edges and corners.
- The 1-g crystals show examples of curvatures caused by fluid flow which are not observed in the low-g crystals.
- Steps or ledges appear more prevalent in the higher-g crystals than in the low-g crystals.
- Twinning is more prevalent as gravity level increases.
- More gas is generated as gravity level increases.

Typical scanning electron microphotographs that illustrate the noted differences are shown in Figures 5 through 11.

The noted differences in crystal structure are undoubtedly the result of different levels of convective vigor at the different g levels. A shadowgraph projection of an electrodeposition conducted on the ground showed convection currents somewhat as illustrated in Figure 12. Similar convective currents accompanying electrochemical silver deposition by copper metal displacement were noted almost a hundred years ago [3,4,5]. One of these early investigators reported that the downward flow originates near the copper, while the upward flow originates at the tops of the silver crystals [3]. It was generally agreed that the downward flow consisted of heavy, copper nitrate reinforced solution, while the upward flow consisted of lighter, depleted silver nitrate solution. It was found that in solutions of less than approximately 3 percent, doubling the silver nitrate concentration caused the rate of silver deposition to increase three times. Above approximately 7 percent, the rate becomes proportional to the silver ion concentration. The rate of deposition for the dilute solutions was found to fit the relationship

$$k = AP^{\frac{\log 3}{\log 2}}$$

where k is the rate of deposition, A is a constant, and P is the proportionate concentration, i.e., P = 1 (0.3542 percent silver nitrate), P = 2 (0.7083 percent silver nitrate). The observed tripling effect on deposition rate by doubling the silver nitrate concentration was dubbed a "2-3 law" at the time. Langley [5], however, explained the "law" as a result of a coupling between a doubled rate of chemical action and 1.5 times convective velocity increase as the silver nitrate concentration doubled.

In further ground experiments during the present study, crystalline structure was found to depend heavily on silver nitrate concentration. For example, Figures 13 through 15 show the types of structure obtained in solutions of various concentration. Three different crystal structures are immediately apparent: (1) a dilute solution (less than approximately 1 percent) gives a mass of spiky, dendritic crystal initially and, after a few hours, a strung-out dendritic streamer that grows downward; (2) solutions of intermediate concentration (approximately 5 percent) give bunched, small crystals that show little growth direction preference initially but will generally develop upward streamers after a time; and (3) concentrated solutions (10 percent and higher) give chunky crystalline streamers that grow emphatically upward and whose microstructure shows evidence of gas generation (Fig. 16). Upward growing streamers, as is well known, are the basis of crystal rock gardens commonly seen in stores as a novelty item.

Increasing g-level at the various concentrations had the effect of producing larger, more coherent downward growing dendrite streamers in dilute solutions and apparently decreasing crystal growth rates somewhat. Stirring of concentrated solutions also appeared to decrease crystal growth rates. Scanning electron micrographs of crystals obtained from concentrated and dilute solutions which had been centrifuged show much the same structural trends as noted for the 5 percent solutions.

Another interesting characteristic of crystal growth in the concentrated solutions is that the upward growing streamers grow along the free solution/air interface when they encounter it (Fig. 17). If the crystal growth is forced to be confined to a surface region, crystal growth will occur along the surface, i.e., the crystals will not grow down (Fig. 18). Growth along an air/liquid interface was also noted in a recent study of the electrolysis of copper from solutions containing an added impurity [6].

The preceding data led to the postulated convection mechanisms shown in Figure 19. In the postulated convection mechanisms, the downward flow of solution reinforced with copper nitrate is assumed to exert a minor influence on convective patterns near crystals growing from concentrated solutions. In concentrated solutions, downward flows occur at sites rather far removed from those where crystals are growing. Furthermore, the downward currents are quite weak during growth from concentrated solutions. Initial upward currents can be seen with the aid of a shadowgraph, while the downward currents cannot. Concentration of convective flows near the tips would require slow growth at the sides of the streamers (Fig. 20). In an experiment in which indifferent electrolyte was added to the nutrient solution (25 percent KNO_3, 25 percent $AgNO_3$), somewhat less upward growth was noted than in solutions without indifferent electrolyte. This result indicates that probably the added potassium nitrate electrolyte decreased the buoyancy of the depleted solution.

The observed growth direction of electrolytically deposited dendrites in solutions is apparently at variance with observations made on dendrite growth in melts. In melts, dendrites grow into a fluid stream [7] (Fig. 21). In the present case, a similar mechanism for downward growth into a convective stream could conceivably arise as the result of bulk solution being brought up to the growing tip to balance fluid loss because of rising currents originating at the growing crystal dendrite. The objection to the postulation of such a mechanism as being determining, however, is that if this mechanism predominated, all of the initial dendrites should develop downward streamers. This does not happen; only a few dendrites near the bottom of a curved wire (Fig. 13) eventually develop downward growing streamers. The data indicate that the upward currents of depleted solution are fairly weak and, therefore, do not result in downward growing dendrites. The downward flowing current of copper nitrate reinforced solution, however, is quite strong – initial downward flows can be seen with the aid of a shadowgraph, while the upward currents cannot. It is concluded, therefore, that downward, dendritic growth results when a few favorably aligned dendrites near the main downflowing convective stream adjust their growth to follow the downward convective current.

Two recent studies of electrodeposition of nickel, cobalt, and iron dendrites [8,9] revealed that dendrites in stirred solutions grow with the convective currents, just as the dendrite streamers in the present study are postulated to do. However, it was determined in the cited studies that the current density at the growth site of such dendrites is unusually high (~20 A/mm^2), much higher than current densities observed if the solutions were not stirred. The latter observation suggests that perhaps a mechanism similar to the one postulated for silver crystal growth in concentrated solutions may have been operative. In the cited studies rather concentrated solutions of cobalt and nickel salts were used.

The fact that crystals grown on top of a concentrated solution and crystal streamers that encounter the gas/liquid interface do not grow downward but grow out along the surface also indicates convection-influenced growth direction. A surface-tension-driven convection accompanying such surface crystal growth probably occurs as shown in Figure 22.

The influence of convection vigor on an overall crystal growth rate is rather unclear at present. In centrifuged and stirred samples at low and high concentrations, crystal growth rates appeared to decrease, although quantitative measurements were not made. Such results, if subsequently confirmed, would be at variance with those reported by Langley in 1884 [5]. Langley found that growth rates in dilute solutions increased with increased stirring or centrifuging. Langley, however, determined the amount of copper dissolved after only 1 minute. The experiments in the present study were run for considerably longer periods. Langley's experiments represent a transient situation, and therefore, do not apply to the present case. The present case is primarily concerned with the steady state currents accompanying relatively long term growth. Other studies in which the rates of silver deposition by displacement of copper, zinc [10], and lead [11] were determined have shown that the crystal growth rates generally increased with concentration and stirring. However, with lead it was found that in solutions above approximately 1N, the rates decreased sharply. In very dilute solutions other anomalies were found. The data, however, are too sparse at this point to undertake even a preliminary elucidation of the influence of convection on overall growth rate.

Alteration of concentration profiles by convection appears to be responsible for the shift from relatively slow to rapid edge growth as gravity level is increased. Convection is believed to decrease the diffusion boundary layer and thereby increase the silver ion concentration near the electrode surface. The shrinkage of the diffusion boundary layer can be postulated thereby to increase electrode potential and current density. In one experimental study [12] it was found that at low current densities, layer crystal growth starts in the interior of the crystal faces, while at higher current densities it starts on the edges and corners.

The noted increase in gas generation during electrodeposition in high concentration solutions and at higher-g levels suggests that convection thinning of the hydrogen ion diffusion boundary layer allows the hydrogen/hydrogen ion couple to operate.

The noted increase in twinning as convective or g levels are increased can probably be explained on the basis of increased mechanical stresses.

SIMILARITIES BETWEEN LOW-G ELECTRODEPOSITION AND LOW-G VAPOR DEPOSITION

An intriguing aspect of electrolytic deposition of metals is that the electrolytic technique possesses many similarities to vapor and solution crystal growth [13,14]. Certain defects obtained using the solution and vapor deposition techniques are also noted in electrodepositions. For example, hopper crystals are often obtained in solution and vapor growth. This sort of crystal arises when growth from the edges and corners is rapid. As the present study shows, convection encourages this type of growth in electrodeposits. It was, therefore, of interest to compare the results of the present study to the results of a Skylab experiment which involved crystal growth by chemical vapor transport [15]. In the cited experiment, germanium selenide (GeSe) and telluride (GeTe) were grown aboard Skylabs III and IV by the following vapor transport reaction:

GeSe (s) or $+ \mathrm{GeI_4}$ (g) GeTe (s)	$2\mathrm{GeI_2}$ (g) $\frac{1}{2}\mathrm{Se_2}$ (g) $\longrightarrow$ or $\frac{1}{2}\mathrm{Te_2}$ (g)	GeSe (s) or GeTe (s) and $\mathrm{GeI_4}$ (s)
Heated End of Test Ampule	Transport Region	Cooled End of Test Ampule

The crystals of GeSe and GeTe grown on the ground were generally dendritic. The differences [15] between GeSe and GeTe crystals grown on the ground and in space can be briefly summarized as follows:

GeSe and GeTe Crystals Grown by Vapor Transport

	Ground Grown	Space Grown
Crystalline Habits	• Partially hollow growth habits • Platelets • Needles • Aggregation frequent • Curved crystals	• More perfect crystalline habits
Defects	• Distorted surfaces • Twinning • Steps and ledges	• Faces show a higher degree of smoothness and crystalline perfection • Edges of crystals better defined

It is indeed remarkable that the list of noted differences between crystals grown by a vapor transport technique on ground and in space is almost identical with a similar list of electrodeposited silver crystals. The similarities, therefore, strongly suggest that the GeSe and GeTe and the silver crystals grew by similar mechanisms and that all were affected in the same manner by convection or the absence thereof.

The question of crystalline sizes obtained in low-g and higher-g levels either by the electrolytic or vapor deposition techniques needs to be addressed because if, as here hypothesized, similar crystal growth mechanisms were at work in the low-g electrolytic and vapor deposition experiments, the growth processes of GeSe and GeTe were more dendritic in low-g than on the ground. It would be expected at first glance, therefore, that a finer, more powdery deposit would have been obtained from the low-g deposition than the ground deposition. Yet, the report on the space-grown GeSe and GeTe implies that the space-grown crystals were on the whole slightly larger than the earth-grown crystals. Such a result, however, on further reflection is not at variance with the hypothesis of more dendritic growth in low-g for the two cases under discussion. The end result of dendritic growth may be a variety of structures depending on a variety of factors [16]. If the dendrite arms are broken off or if a multitude of dendrite stalks are nucleated simultaneously, small, powdery crystals would result. If, however, only a few dendrite stalks are nucleated and sufficient time is allowed for the spaces between the dendrite branches to be filled in, single crystals of substantial proportions can result. In both the electrodeposition and vapor deposition experiments no control of nucleation frequency was exercised. The size of the crystals obtained in the two cases, therefore, is not a significant detraction from the hypothesis of predominantly dendritic growth in low-g in both cases.

It is also of interest to note that a higher mass flux was obtained in the vapor experiment in low-g than was expected. Interestingly enough, Commander Carr reported 1 day after inserting the copper wire into the silver nitrate solution that the silver crystals were "growing beautifully." His statement implied that appreciable growth had occurred in 1 day. This was somewhat surprising because appreciable crystal growth of the ground samples was not evident.

The higher low-g mass fluxes may have been the result of a nongravity-driven form of convection. It may be well to note here for the benefit of those who are unfamiliar with low-g environmental effects that convection does not necessarily go to zero in low-g environments. Low-g can drive appreciable convection if container grometry or temperature gradients are appropriate. Also, convective driving forces other than gravity may be operative. The kinds of convection and other fluid motions that are possible in low-g environments have been recently reviewed [17,18]. Appendix B summarizes a convection analysis of the vapor transport experiment under discussion, assuming gravity as the only driving force. This analysis, however, concludes that for the given cell geometry and temperature gradients of the vapor transport experiment the low level of gravity prevailing at the time of the experiment was insufficient to drive convection of any appreciable vigor. Another explanation of the unexpectedly high mass fluxes is that perhaps the forward movement of the dendrite tip, generally neglected, accounts for the discrepancy between the observed mass fluxes and those calculated on the basis of diffusion. This shortcoming of dendrite growth theory was pointed out a number of years ago [19]. The question remains for future studies to resolve.

The preceding data indicate that massive, almost perfect crystals can be grown (by electrodeposition, vapor deposition, and presumably solution growth) in low-g environments by employment of either high supersaturations or low supersaturations with strict control over nucleation frequency. The topics of nucleation mechanism and frequency and breakdown of a flat, smooth interface into a dendritic interface are beyond the scope of the present study. Some practical methods by which nucleation frequency can be controlled, however, can be mentioned. For example, in electrodeposition the current density or potential, two important parameters of nucleation frequency, are readily controlled. In vapor deposition, methods which might be employed are the introduction of heterogeneous catalysts or a seed crystal. At present the advantages of growing massive crystals via the dendritic route are not obvious, but further reflection may reveal overlooked factors.

ELECTRODEPOSITION OF FILMS, RIBBONS, AND FIBERS

It was often the case during the course of the ground studies that electrodeposited silver crystals were left standing in contact with their mother liquor for weeks. Almost invariably such crystals would develop new crystal forms consisting of ribbons, long thin strands, and in a few cases thin foils or films (Figs. 23, 24, and 25). The film or foil of silver shown in Figure 25 was obtained by electrolysis in an earlier study [20]. The intriguing aspect of these types of growth is that possibly germanium and silicon can also be electrodeposited in such forms from nonaqueous solutions. Direct production of germanium and silicon in thin, single crystal foils would undoubtedly help to bring down the price of solar photocells. It is generally known that much activity is occurring at present in trying to perfect the method of pulling silicon ribbons from the melt. The basis of this method is initial formation at a melt surface of two silicon dendrites which are co-planar. The two dendrites are then slowly pulled from the melt. The melt between the dendrites solidifies to give a single crystal ribbon.

The possibility of considering electrolytic growth of germanium ribbons arose as follows: Faust and John in 1961 [21] suggested that silver, lead, and copper dendrites grow electrolytically at low current densities by a twinning mechanism similar to that found for melt-grown dendrites of germanium, silicon, and the III-V intermetallic compounds. Presumably, germanium and silicon dendrites would grow by the same mechanism electrolytically. The electrochemistry of germanium and silicon, however, has not been extensively studied. In aqueous solutions low hydrogen overvoltages and various other undesirable side reactions result in poor deposits. Lustrous deposits of germanium from nonaqueous solutions, however, have been obtained [22]. The possibility of directly producing germanium or silicon ribbons electrolytically may have occurred to the earlier cited investigators, but apparently no one has pursued the matter further.

IMPLICATIONS FOR TECHNOLOGICAL APPLICATIONS

The preceding data and discussions indicate that a low-g environment can serve to increase control in the electrodeposition, vapor deposition, and solution techniques. In particular, it appears that the following products can be more advantageously grown in low-g environments than in 1-g environments:

- Finer powders with more perfect microcrystalline structures
- Massive, single crystals with fewer imperfections.

The realization of these advantages, however, requires further studies into practical means of controlling nucleation rates.

Catalysts appear as promising applications for low-g grown powders. It has not been discussed, but electrodeposition of alloys is also possible. Fine powders of these may also have desirable catalytic properties. The influence of crystal structure on catalytic effectiveness, however, is beyond the scope of the present study. Uses for massive single crystals of semiconductors and optical materials are well known.

The phenomenon of electrodeposition along a gas-liquid interface discovered in the present study as well as that reported recently in the literature [6] may provide one basis for growing thin films of metals and perhaps semiconductors also directly by electrolysis. Ribbons and films grown in solution by electrolysis may be another basis for growing semiconductor films directly. Ribbons of metals and semiconductors can perhaps also be grown by pulling a dendritic cathode from aqueous solutions. Thin ribbons or films of semiconductors would find a ready market for electronic substrate and photocell applications. Additionally, centrifuge-grown crystals with numerous imperfections may find applications also in the field of catalysts.

CONCLUSIONS AND RECOMMENDATIONS

On the basis of the data obtained from space and ground experiments, the following has been concluded:

- The rate of electrochemical displacement of silver ions from a 5 percent aqueous solution by copper is predominantly diffusion controlled in space and kinetically controlled in 1- and higher-g because of augmentation of mass transport by convection.

- Downward and upward growing crystal streamers are the result of gravity-driven convection, the flow patterns of which can be delineated. Lateral growths along an air/liquid interface are the result of surface-tension-driven convection, the pattern of which also can be delineated.

- Electrolysis in space or low-g environments can produce either dendritic crystals with more perfect microcrystalline structures or massive, single crystals with fewer defects than those grown on ground or at higher-g levels.

- Vapor transport growth of GeSe and GeTe is affected by convection mechanisms similar to the mechanisms hypothesized for the electrochemical deposition of silver crystals.

- Thin ribbons or films of semiconductors would find a ready market for electronic substrate and photocell applications. Centrifuge-grown crystals with numerous imperfections may find applications in the field of catalysis.

The conclusions and implications of the present study need to be tested by techniques more controllable than electrochemical displacement. Appendix A lists some of the shortcomings of electrochemical displacement as a technique for elucidation of crystal growth mechanisms. Tests utilizing an electrolysis cell with silver anode and cathode and in which the current density and potential can be either controlled or monitored while the electrolysis is proceeding are called for. Obviously, further space experimentation is highly desirable. In particular, the present investigators should dearly like to grow silver crystals in space from very concentrated solutions. Highly desirable also are growth rate studies at various g-levels and flow visualization studies of the convective currents accompanying crystal growth. Because dendrites and crystal streamers are fairly small and the flows, therefore, fairly localized, some very sensitive technique such as laser interferometry may be required to see flow details. Other needs are: experiments on vapor transport deposition, especially ones utilizing higher-g levels; testing of the applicability of the present conclusions to solution crystal growth; more information on nucleation processes and possible convection effects thereon in electro, vapor, and solution growth; and more research on the electrodeposition products of germanium, silicon, and other semiconductors.

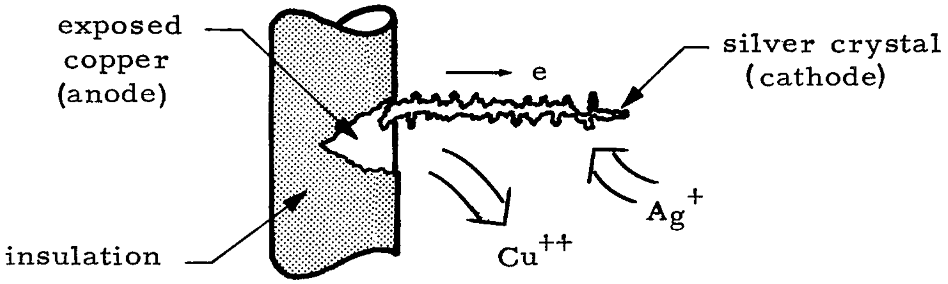


Figure 1. Mechanism of electrochemical displacement of silver ions by copper.

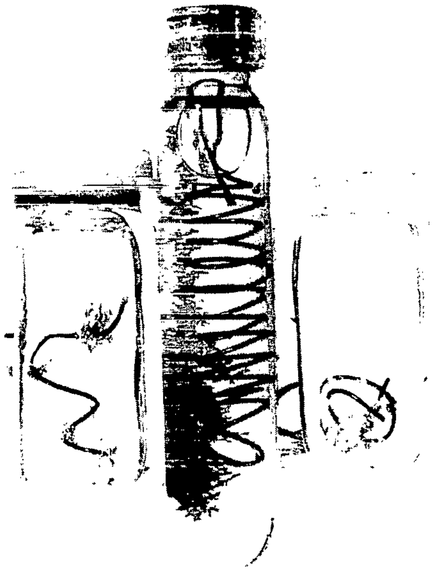


Figure 2. Silver crystals electrodeposited in space and on earth. Center tube (8.25 X 1.6 cm) contains flight-grown crystals; side flanking vials contain crystals grown on earth for the same length of time.

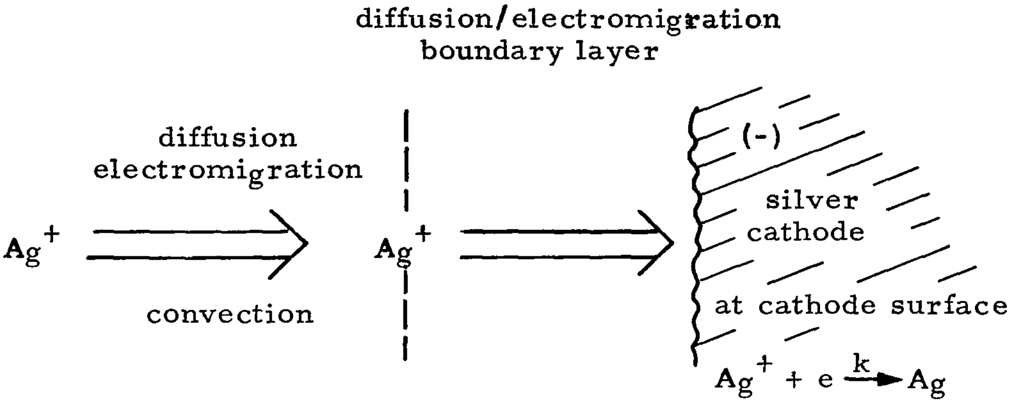


Figure 3. Various rate processes involved in silver ion deposition.

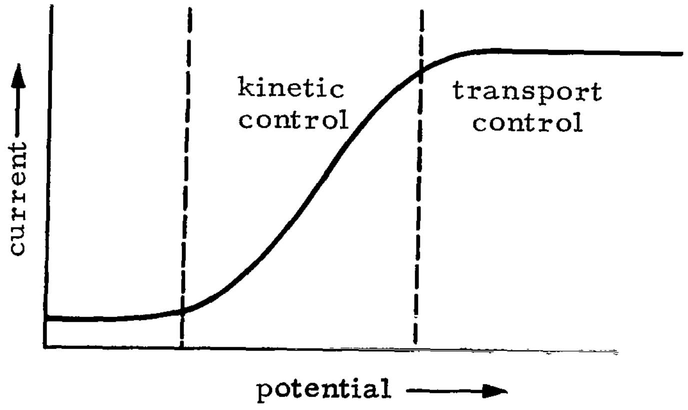


Figure 4. Illustrative current-potential curve.

Figure 5. Silver crystals grown in space from 5 percent solution (illustrating more perfect microcrystalline structure).

Figure 6. Silver crystals grown in space from 5 percent solution (illustrating sharp edges and corners).

Figure 7. Crystals grown from 5 percent solution on earth at 1-g (illustrating rapid growth from edges and corners and also curving of crystals).

Figure 8. Crystals grown from 5 percent solution on earth at 1-g (illustrating curving of crystals).

Figure 9. Crystal grown from 5 percent solution at 5-g (illustrating hopper growth).

Figure 10. Crystal grown from 5 percent solution at 5-g (illustrating ledges or steps and rapid growth from corners and edges).

Figure 11. Crystal grown from 5 percent solution at 5-g (illustrating imperfect structure and evidence of gas formation).

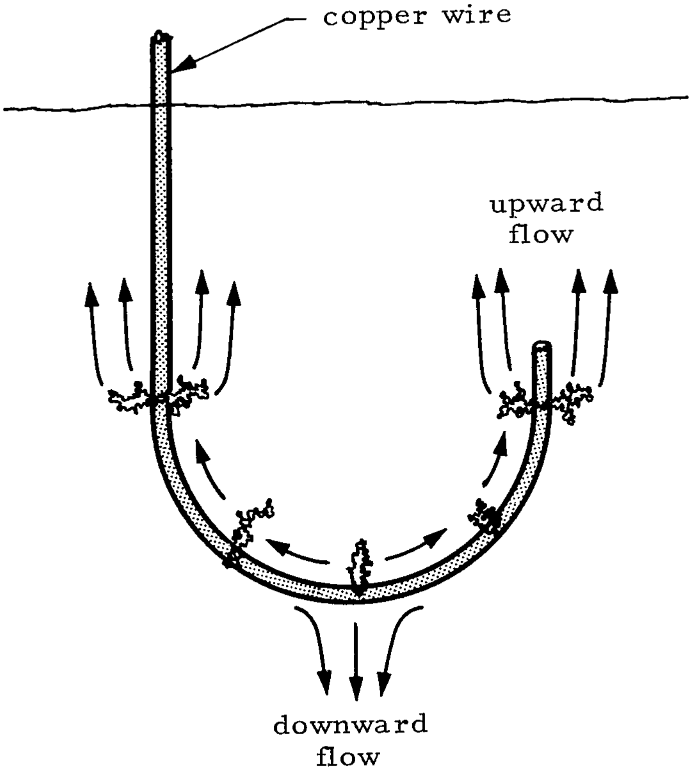


Figure 12. Schematic of convection currents seen with shadowgraph during crystal growth from 5 percent aqueous solution.

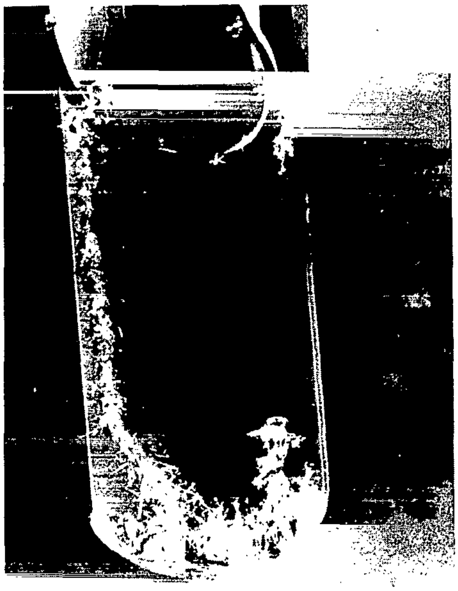


Figure 13. Downward growing dendrites on ground 0.4 percent solution concentration.

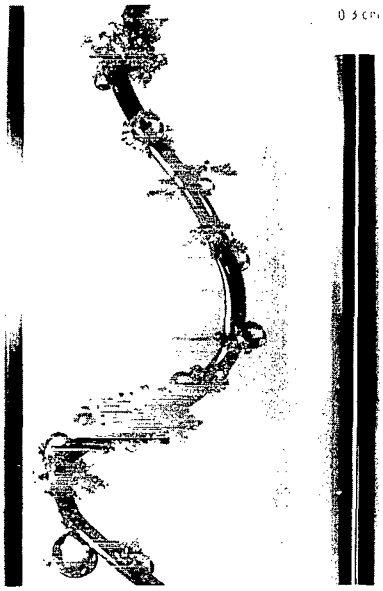


Figure 14. Silver crystals growing from a 5 percent solution on the ground.

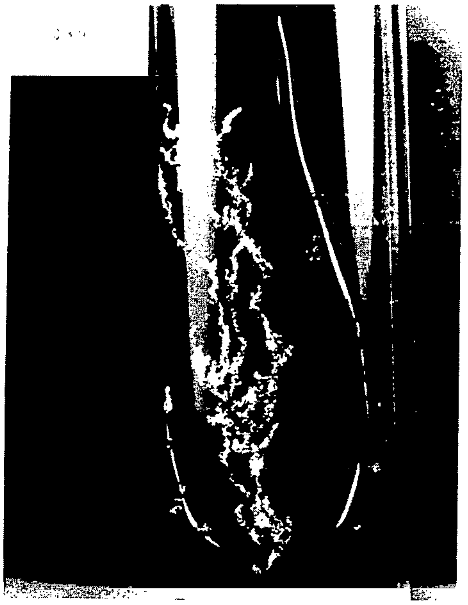


Figure 15. Upward growing streamers on ground 50 percent solution concentration.

Figure 16. Crystal grown from 30 percent solution (illustrating gas generation).

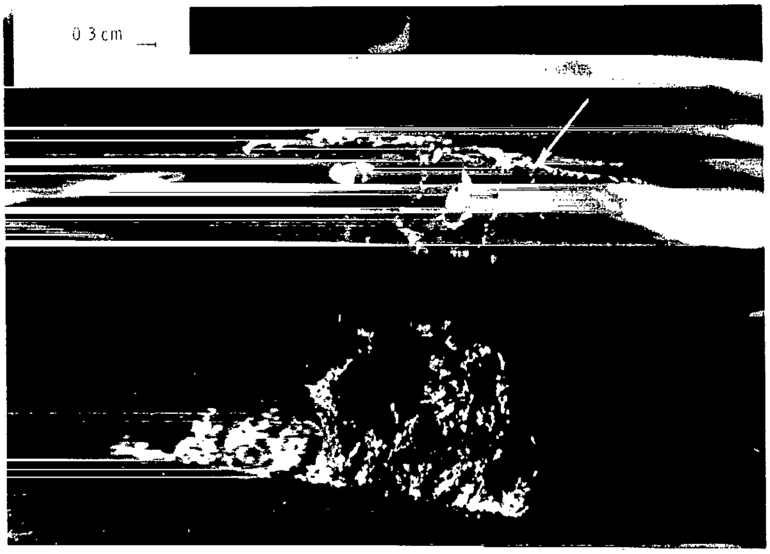
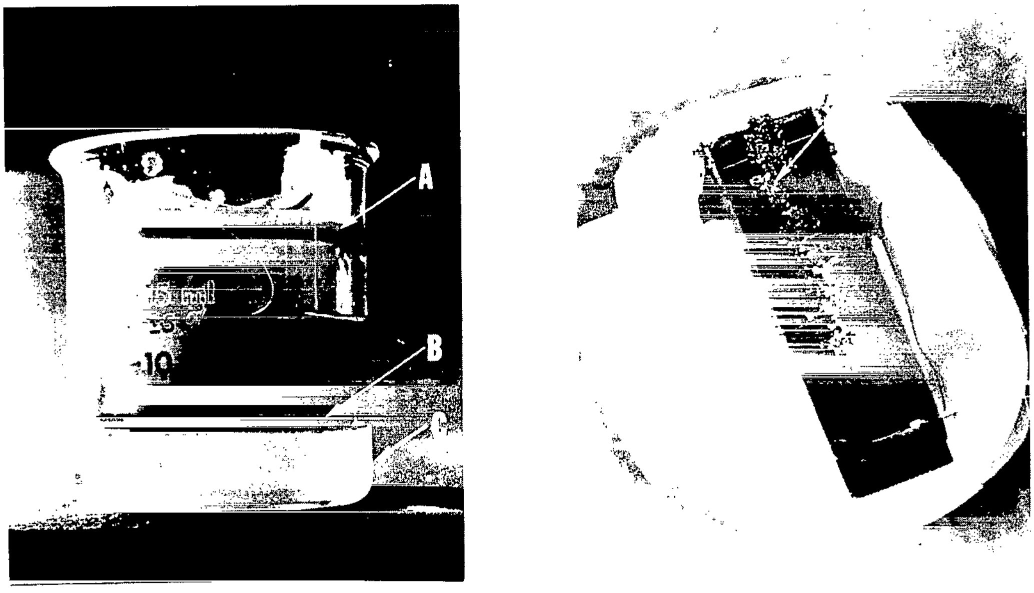


Figure 17. Radial growth along an air-liquid interface. (The liquid level was lowered to show radial growth along surface.)

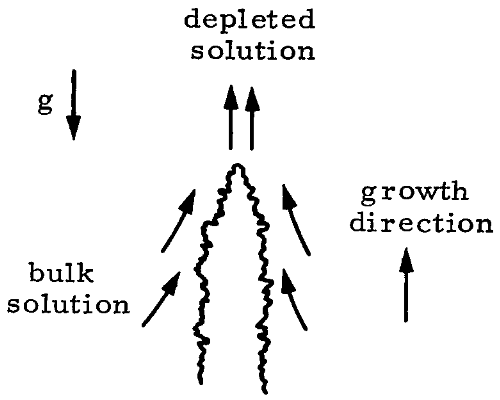


a. Side view (A - stopper, B - copper plate with growing crystals, C - solution).

b. Bottom view.

Figure 18. Crystals growing at top of solution.

a. Concentrated Solutions - Kinetic Growth



b. Dilute Solution - Dendritic Growth

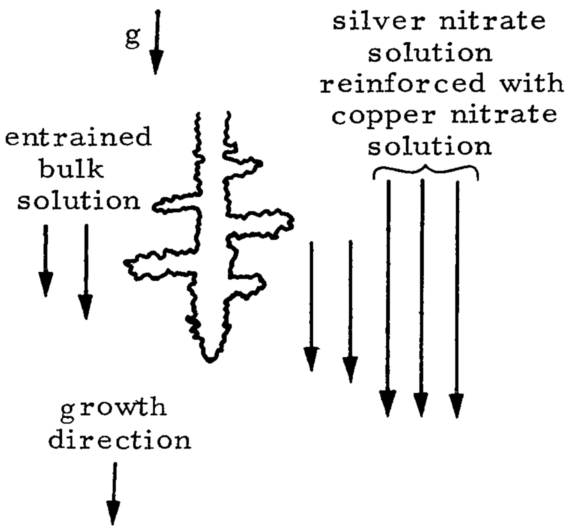


Figure 19. Schematic of crystal growth and convection patterns in dilute and concentrated solutions.

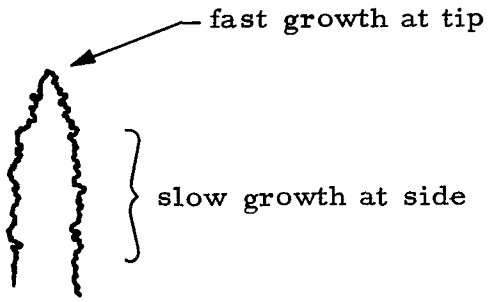


Figure 20. Schematic indicating regions of differing growth rates in upward growing streamer.

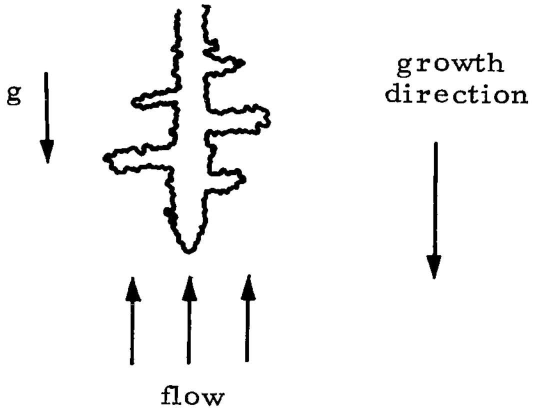


Figure 21. Convective flow in dendritic growth from melt.

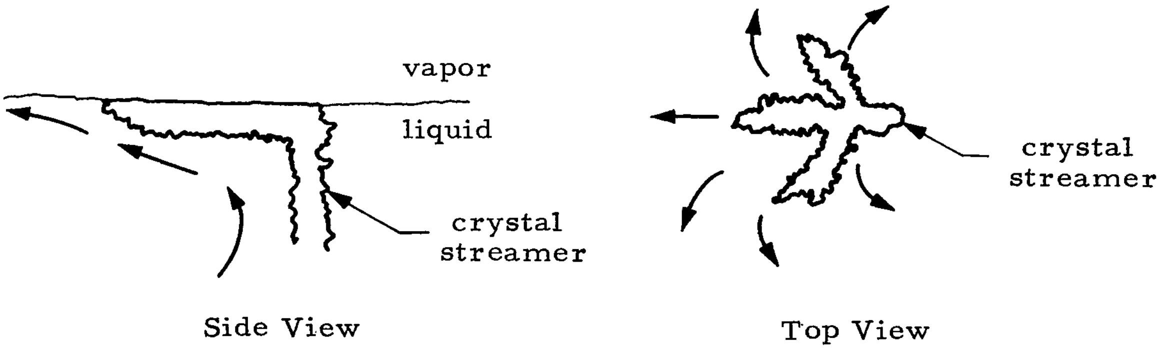


Figure 22. Schematic of surface tension flow accompanying crystal growth at liquid/gas interface.

Figure 23. Electrodeposited silver crystal ribbon.

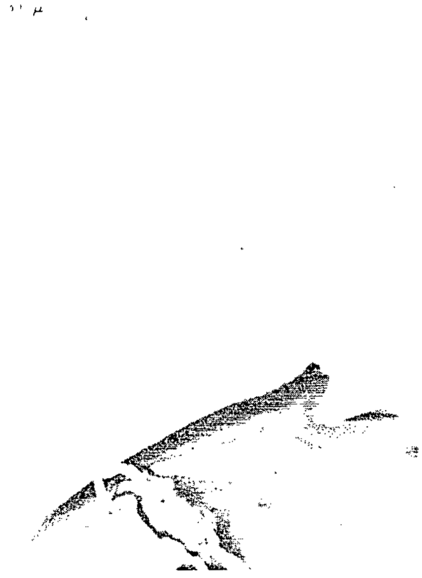


Figure 24. Electrodeposited silver crystal fiber.

Figure 25. Silver crystal film electrodized from 0.5 M $AgNO_3$ solution (film less than 1 mil thick). Photo courtesy of John P. Young, National Bureau of Standards.

APPENDIX A

EXPERIMENTAL DETAILS OF SKYLAB DEMONSTRATION TV106 – ELECTRODEPOSITION OF SILVER CRYSTALS

Experimental Materials, Procedures, and Conditions

The following is a summary of the materials and conditions employed in performance of the flight experiment:

Container:	10 ml Lexan centrifuge tube with polyethylene screw top and an O-ring gasket of Buna N rubber containing carbon particles
Silver nitrate:	Merck C. P. (Product 12C82, lot. 71731)
Copper wire:	Belden insulated wire (LE8051 22 Awg Sgl Beldsol, polyurethane and nylon insulation) Belden Corporation, Chicago, Ill. 60644
Water:	Distilled water of unspecified purity
Cabin temperature at time of experiment:	~22°C (72°F)
Cabin pressure:	5 psi
Composition of silver nitrate solution:	5% by weight (9.5 ml of solution made by adding 0.5 g $AgNO_3$ to 9.5 ml of water)
Date of experiment:	January 24, 1974
Date of solution preparation and packaging (in Houston, Texas):	November 1, 1973
Date of re-entry:	February 8, 1974
Date of receipt by investigators of experiment package and removal of crystals from solution:	February 11, 1974
Solution preparer:	Person A
Radiation dose:	Significant, as judged by color change of initially clear Lexan

Flight Experimental Procedure

1. Coil copper wire around pen (minimize finger contact with wire) to fit within the solution volume of container, leaving a wire tip for inserting wire in solution without the fingers contacting solution (coil diameter should be smaller than container to assure minimum coil/container contact).

2. Using pocket knife lightly cut wire insulation several times to provide nucleation sites for crystal growth. (Areas of cut to be small; do not abrade wire, nick insulation.)

3. Centrifuge container to settle solution. WARNING – Avoid skin contact with solution (5 percent silver nitrate).

4. Wrap tissues around cap and remove cap very slowly to allow pressure equalization and insert wire into solution.

5. Replace cap and restrain container for later photographing.

6. Photograph crystals in vial after approximately 6, 24, and 76 hours. Camera setup: Nikon (per photo PAD), 5 mm - K1 adapter (F2.8, 1/30 s) manual focus. Lighting – Hi intensity light with vial orthogonal to axis of light to minimize reflection.

The experimental conditions prevailing for the ground preparation of silver crystals for comparison to the flight grown crystals are as follows:

Containers:	Glass vials
Copper wire and silver nitrate:	Same as used for flight test
Water:	Distilled water of unspecified purity
Temperature:	Room (~22° – 24°C)
Composition of silver nitrate solutions:	5% by weight (~10 ml used in each of these preparations)
Pressure:	1 atm
Date of experiment (Huntsville, Alabama):	January 24, 1974
Date of solution preparation (Huntsville, Alabama):	January 15, 1974

Date of removal of silver crystals from solution:	February 11, 1974
Solution preparer:	Person B

When the flight silver crystals were received February 11, 1974, they and the ground samples were removed from solution, washed with distilled water four times, and dried in a dessicator overnight. Approximately 0.3 g silver crystals were obtained from the flight test. A chemical analysis by emission spectroscopy gave the following results:

Chemical Analysis of Spent Solutions

Sample	Ag	Cu
Flight	2.0	9300
Ground Test 1	12.0	8900
Ground Test 2	10,000	6400

Trace quantities Fe, Mg, Si, Al

Original solutions before insertion of copper wire would have contained approximately 3 X 10^7 μg/l Ag and 0 μg/l Cu. If all of the silver had been replaced and no other reactions occurred, copper concentration should have been approximately 6 X 10^6 μg/l. The data show that other reactions occurred. This is not the only evidence for additional reactions. In addition to silver crystals, small amounts of blue and dark red crystals of unidentified materials are obtained in any ground electrochemical displacement of silver ions by copper. Such blue and red crystals were also obtained in the flight experiment. Further analyses of these colored crystals, however, were not undertaken. The somewhat higher silver ion concentration in the two ground samples lends credence to the impression mentioned in the text of faster crystal growth rates in space than on the ground.

Further ground tests involving concentration variations and centrifuging were accomplished utilizing silver nitrate of reagent grade (Baker analyzed 3426, Lot. 31522) but somewhat decomposed, as evidenced by the dark color. The copper used in these tests was generally the same as used in the flight test.

The apparatus used for centrifuging utilized a dc magnetic torque motor, low-noise electrical slip ring, dual-pen recorder, programmable power supply, and a period sensing network. A free swinging cannister which contained the sample and a counterweight were suspended from the centrifuge arms by a pivot to ensure that the acceleration force was always along the long axis of the sample tube; i.e., in the same direction as gravity when the tube stood upright.

Shadowgraph equipment consisted of some improvised flat plate cells and a high intensity microscope light. White paper served as a screen.

Control or Error Analysis

Because of the conditions under which the flight experiment was developed and performed, the degree of control of the experimental solutions and procedures was not what might have been achieved under more favorable circumstances. It is of interest, therefore, to inquire what errors or lack of experimental control might have influenced the interpretations and conclusions presented in the main body of this report.

One of the chief concerns of the study was the question of whether continued growth after re-entry would mask the crystal growth that occurred in space. A procedure having the astronaut remove the silver crystals while still in flight was judged too time consuming, complicated, and risky to pass a review. Ground tests indicated that most of the growth occurred in approximately 3 days. The TV106 experiment consisted of 15 days of crystal growth in space and 3 days on the ground after re-entry. When the crystals were received in Huntsville, Alabama, they were a loose, coarse powder. At what point the crystals had been dislodged from their growth sites is not known, however, during re-entry would appear as a likely time. In any case, the scanning electron micrographs of the flight crystals which show significantly different structures allow the conclusion that continued earth growth after re-entry did not mask the space growth.

Another concern was that perhaps impurities were introduced into the flight samples which were not present in the ground samples or vice versa. A review of the experimental conditions for the flight and ground samples shows that ample opportunity existed for such an occurrence: i.e., different people prepared the flight and the ground samples, the water used to prepare the flight and ground samples came from different sources, different people performed the flight and ground experiments, and the containers used in the ground and flight experiments were different. Also, the flight sample received an apparently appreciable dose of radiation. However, the fact that self-consistent trends could be established using not only data from the flight crystals but also from ground and centrifuge studies (in some of which another grade silver nitrate was used) indicates that lack of control over impurities was not an appreciable error.

Finally, errors such as variations in volume of solution used for any particular test and day-to-day temperature variations were judged insignificant because many tests were done under a variety of volume and temperature conditions, and again, self-consistent trends traceable only to convection effects could be established.

Deficiencies of Electrochemical Displacement Technique for Quantitative Crystal Growth Studies

Although the electrochemical displacement technique proved useful for purposes of an easy, safe flight demonstration experiment and supplying qualitative data on the nature of crystal growth in space, a number of serious objections to its use for further quantitative studies exist: no control or knowledge of current and potential during crystal growth; possible kinetic effects in the anodic dissolution processes; introduction of another ionic species into the solution by electrochemical reaction; no control or knowledge of the area of reaction; and the presence of extraneous side electrochemical reactions. For demonstration purposes and for student experimentation, however, the electrochemical displacement technique offers numerous obvious advantages.

APPENDIX B

CONVECTION ANALYSIS OF SKYLAB EXPERIMENT M556 (VAPOR GROWTH OF IV-VI COMPOUNDS)[1]

A numerical analysis was conducted of three configurations (Fig. B-1) containing GeI_4 gas at 1.5 atm. The further boundary conditions utilized were as follows:

Hot Temperature: 520°C

Cold temperature: 420°C

Mean gravity level: 2×10^{-4} g_e (where g_e is the gravitational acceleration on the earth surface, 980 cm/s^2)

Results

The results of the analysis are presented in Figure B-2 which shows that the fluid velocities are quite small and that the heat transfer is negligibly affected.

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[1] Lawrence W. Spradley, Lockheed Missiles and Space Company, Huntsville, Alabama, performed the analysis.

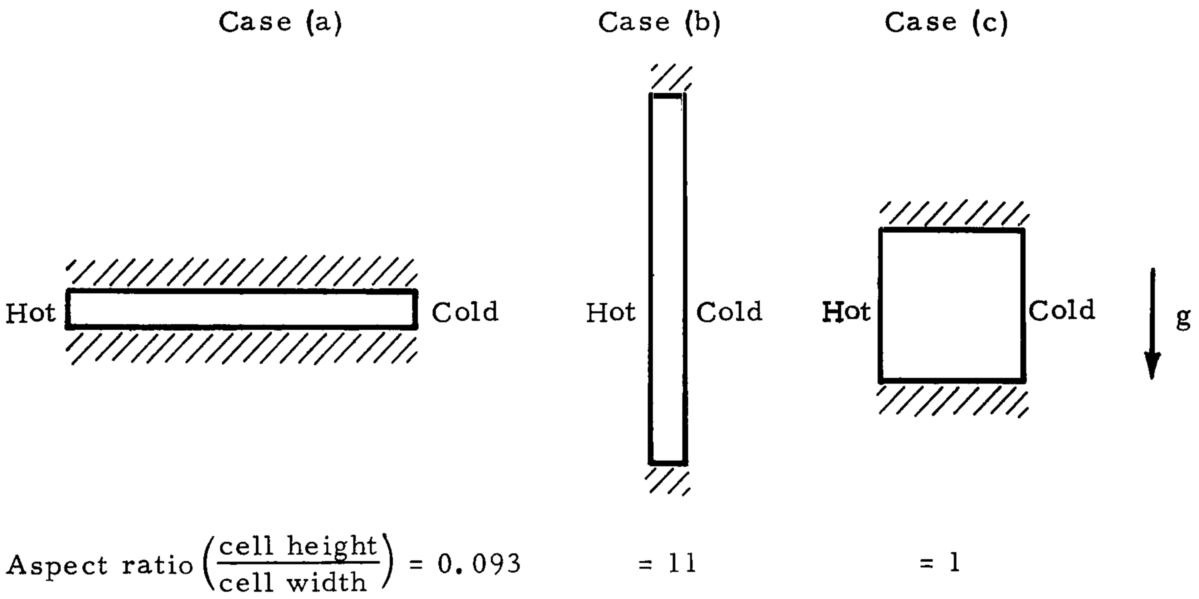
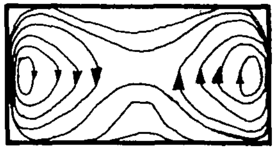
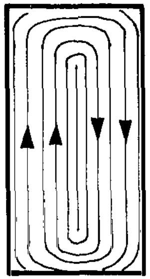
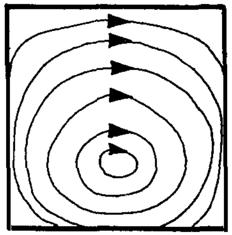
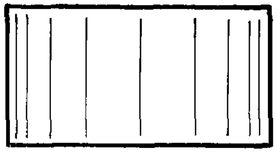
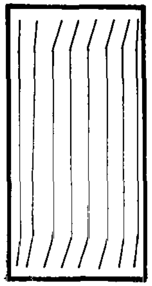
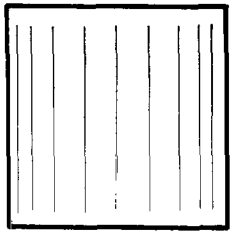


Figure B-1. Configuration utilized in the convection analysis of the Skylab M556 Experiment.

	Case (a)	Case (b)	Case (c)
Calculated Maximum Velocity	0.0025 cm/s	0.014 cm/s	0.072 cm/s
Nusselt Number*	1.000	1.004	1.008
Flow Pattern**			
Temperature Profile**			

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* The Nusselt number is the ratio of actual heat transferred to heat transferred if conduction were the only process by which heat could be transferred.

** The aspect ratios have been altered to allow adequate space for drawing in the streamlines. The lines shown in the temperature profiles are isotherms. Case (a) represents convection after 800 s. The other two cases are steady state situations.

Figure B-2. Results of a convection analysis of the Skylab M556 Experiment.

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