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CRYSTAL SYNTHESIS BY REFRIGERATION

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ABSTRACT

Maser operation requires crystals containing paramagnetic ions such as chromium or nickel in minute percentages which substitute generally for cobalt, aluminum, or magnesium. Crystals of K_3 $(Co_{0.995}Cr_{0.005})(CN)_6$ have been grown in freezer compartments at temperatures of 4° to 5° C. Seeds for crystals are inserted in solutions which are saturated at ∼0° C. in the freezer. Controlled quantities of solutions which are saturated at room temperature are periodically introduced into the freezer solution. The desired effect is that the growing crystals will adsorb all precipitating ions above the saturation level to eliminate additional spontaneous seeding. Daily turning of the crystals is conducive to homogeneous growth. Growth rates have been measured. Small crystals have a faster growth rate per unit weight but a lesser mass accumulation per unit time than larger crystals. Space restrictions are the only limitations on the maximum size that can be developed. Single crystals as large as: $c=12$ cm., $b=4$ cm., $a=3$ cm. have been prepared during a three month growing period.

INTRODUCTION

In the development of a device that would produce *M*icrowave *A*mplification by *S*timulated *E*mission of *R*adiation, now known as a *MASER*, paramagnetic crystals of various types can be used. Dr. J. W. Meyer of the Lincoln Research Laboratories of the Massachusetts Institute of Technology made a thorough analysis of what atoms would be best suited in a MASER crystal, and chromium was indicated as being one of the most desirable. Upon searching through the literature for chromium bearing crystals he chanced on the isomorphous series of K_3 (Co, Fe, Cr) $(CN)_6$. These crystals had been grown from solution; their crystallography was known; and the amount of chromium that could be introduced could be rigorously controlled. Dr. Meyer asked Dr. Harry Gatos, also of Lincoln, to prepare crystals of the composition K_3 $(Co_{0.995}\ Cr_{0.005})$ $(CN)_6$. Shortly thereafter the author was consulted concerning the preparation of such crystals, and three different methods were initiated, all of which were successful, but only one of which will be considered here, synthesis by refrigeration.

A normal household upright refrigerator was used in the first synthesis in the Boston University Laboratories and at Lincoln. Several disadvantages of the upright refrigerator became apparent; and when the author was contacted by Dr. Harold I. Ewen and Mr. William From of the Ewen Knight Corporation of Needham to prepare comparable crystals with various chromium contents, a switch over to the horizontal freezer type of refrigerator was made. Miss Irita Vilks was engaged by Ewen Knight to do the actual synthesis under the direction of the author, and the results of this program follow.

Basic Philosophy of the Refrigeration Technique

Although crystals can readily be grown by evaporation of a saturated solution, two major problems often arise when such a technique is used. The first of these, the excessive precipitation in the meniscus region between the solution and the beaker with subsequent capillary flow in the precipitate and further precipitation until, if permitted, the inside and outside walls of the container are covered with precipitate, can be controlled by lining the container with a non-wetting agent at the junction region between the surface of the solution and the container. This procedure is often unsatisfactory, and the operator is compelled to change containers periodically. Other difficulties with the non-wetting agent are often encountered. Obviously, then, crystallization without evaporation is desirable.

The second major difficulty with crystallization by evaporation is the customary over seeding, particularly in the surface tension film at the surface of the solution. Since this area, along with the meniscus region are the only places where supersaturation initially occurs, excessive seeding occurs. The density of the surface tension layer, for all practical purposes, is very high, witness the floating of a greased needle on water; and the newly formed seeds may grow to considerable size while floating at the surface, even though their density far exceeds that of the solution as a whole. Hopper shaped crystals comparable to those formed in saline water bodies gradually develop. Periodically these sink to the bottom in random orientation with the crystals already lying on the bottom, and the total result is a chaotic arrangement of many small crystals. This difficulty can also be controlled in part, but excessive seeding is one of the major problems of crystal synthesis by evaporation.

Since single, homogeneous crystals approaching maximum sizes of 40–50 mm. were desired for the maser experimentation, the use of the evaporation technique seemed undesirable. It is, of course, well known that solubilities of most substances differ at different temperatures, and it was decided to use the temperature differential method of synthesis. Solutions were kept in a bath at 40° C. in the Lincoln Laboratory, and periodically some of this stock solution was added to the crystal growing bath at 30° C. The bath was covered with a perforated plate reducing, but not completely eliminating, evaporation. Seeds, mounted on pedestals, which will be described later, picked up the excess ions developing from the temperature differential. Both stationary and moving seeds were employed in this phase of the synthesis program. Although most of the disadvantages of the evaporation technique were eliminated by this approach, the problems involved in maintaining bath temperatures, in controlling weekend growth, and others made the use of this technique of crystallization somewhat unattractive.

Simultaneously with the above approaches to synthesis the same basic approach of crystallization by *thermal differentiation* was begun under refrigeration conditions. A common upright type of household refrigerator was employed; in this refrigerator the beakers were placed which were to hold the host solution in which the crystals were to grow. Feed solutions at room temperature were kept available, and periodically small amounts of these solutions were added to the host solution. The general philosophy of approach suggested that the thermal differentiation would produce an excess of ions over saturation. If the feeding process were adequately controlled, all excess ions would precipitate on the seeds; no new nucleii would form; and the rate of growth would depend on the rate that ions could be added which could be concomitantly absorbed.

TECHNIQUE OF CRYSTALLIZATION BY REFRIGERATION EQUIPMENT

The first refrigerator employed was the normal upright type; and although excellent crystals were grown in it, certain disadvantages such as wide temperature variations during open and shut phases of operation suggested that the horizontal freezer type of unit could be better employed. The opening of such a chest at the top inhibited the flow of cold air from the chest, and manual operation of crystal turning in the chest and of crystal feeding could be done without a marked temperature variation. The temperature of operation of the chests was in the region $-4°$ to $+5°$ C. at the bottom of th chest. The temperatures in the higher part of the chest were as much as 10 degrees warmer than at the bottom.

The stock solutions were composed of 150 grams of potassium cobaltichromi cyanide in 450 grams of distilled water. This yielded a solution which was not saturated at room temperature but which was significantly supersaturated at refrigerator temperatures. The solubility curves will not be reproduced here. A magnetic stirrer was used to facilitate solution. The preparation of the *host solution* in which the crystals would grow involved two steps. Thirty cubic centimeters of stock solution were placed in a beaker and introduced into the refrigerator. Seeding very quickly took place. After the solution had stood an adequate time to permit complete equilibrium to be established, the solution remaining in the beaker was decanted into another previously cooled beaker and was set back into the refrigerator for observation to make sure seeding was completed. If it were not, the process was continued until the host solution was free and remained free of all seeds.

The procurement of seeds to be placed in the stock solution was made in several ways. The crystalline mass that precipitated when the stock solution was placed in the refrigerator was inspected, and the better crystals were separated from the remainder of the mass. Care was required that no foreignly oriented material was present on the selected seeds. Crystals of two or three habits could sometimes be found in the crystalline mass, but the general tendency was for all crystals to have essentially the same habit. Since it was discovered that the final habit of the crystals could be largely controlled by the habit of the seed crystal, considerable effort was employed to find seeds with the desired initial habit. Seeds were also produced by evaporation of the stock solutions under vacuum and in the open air. The best seeds were obtained early in the evaporation process before many nucleii had developed. Seeds less than 1 mm. in maximum dimension were often employed. One of the most successful seed production methods was that of crystallization from a residue film from an emptied beaker in which the solution had been standing. After pouring the solution from the beaker, the beaker was left to stand without washing, and a few isolated crystals formed on the beaker bottom or walls. These were usually of the habit desired in the final crystals.

Once the seeds were selected they were handled with plastic forceps to eliminate fracturing because of differential thermal expansion when held in the hands. The fractures were never sufficiently large to cause a break-up of the crystals, but they did cause the development of cloudy zones in the growing crystals. Whenever it was necessary to handle the crystals with the hands, rubber gloves cut down heat conductivity to the crystals. It was important that the crystals not undergo any strong temperature variation, and to this end the crystal seeds were inserted on filter paper into the chest and were cooled until they were the same temperature as the host solution. Cooling by this method was less shocking than by direct insertion from the outer warm air into the cold host solution.

In order to eliminate the possibility of subsequent seeding on the seeds, the crystals were mounted on pedestals to keep them off the bottom; the sizes of the pedestals varied with the size of the growing crystals. The greatest difficulty in controlling seeding was always in the very early phases of growth. At this stage, although the individual seeds grew proportionately very fast, it was impossible to add such a small quantity of stock solution that the seeds in the host solution could adsorb all of the precipitating ions as they were available, and some random seeding was the common result. This could be eliminated in part by placing many seedlets in the same host solution and, aside from the mechanical problems of keeping the seedlets on the pedestals, this technique kept foreign seeding at a minimum. Once the crystals reached maximum dimensions of three or more millimeters, they were easily handled, and non-desirable seeding could be completely controlled. As the crystals grew to larger dimensions, they were placed on larger pedestals. When all danger of seeding was past, the crystals which were 1 cm. in at least one direction could be placed directly on the base of the container. The larger the crystals became, the fewer seed units were kept in any one container, for there could be a complete pick-up of all precipitating ions on the larger surfaces of the fewer crystals.

The feeding of the crystals was practically as simple as the feeding of animals. By simple experimentation it was possible to determine how much stock solution could be added daily and be utilized by the growing crystal. Since evaporation was practically negligible from the host solution, the general practice was to remove practically as much solution daily before feeding as was to be added. This kept the degree of saturation upon the addition of stock solution practically constant. The quality of crystallization depended largely on the rate of feeding and on the practices employed in handling the crystals. The general practice we adopted was to feed the crystals three times a day with particular care not to overfeed before the long night period when no attention could be given the crystals. Pipettes and droppers were used for feeding upon occasion. Hollow glass tubes with the finger capping one end to keep the solution within until brought to the host solution were also used. Micro-graduated flasks were used in special control cases where the rate of addition and crystal growth were being carefully checked.

At the peak of crystal synthesis by the above technique at the Ewen Knight facility as many as 400 crystals were being grown simultaneously in beakers and other containers in two freezer units. The beakers were held in trays, with one tray superimposed over another to depths as great as four or five trays. The beakers were labeled as to the percentage of chromium which was present in the solution, and as the crystals reached sizes adequate for maser experimentation, they were removed from the solutions and properly stored.

Turning of the crystals at least once a day proved both desirable and necessary when good quality crystals were desired. This was true both when the crystals were mounted on pedestals and when they were on the beaker bottoms. Crystals set on pedestals grew around the pedestals and enclosed them unless turned. If turning were not frequent enough, the impression of the shape of the pedestal was left on the supporting crystal face, and this impression was often difficult to eliminate. Crystals which lay on the beaker floor developed a large, non-smooth concavity on the floor side unless turned periodically. Generally, a turning of once a day was adequate.

One point of interest arose during checking of the effects of turning. It was stated earlier that the habit of the adult crystal was to a large degree determined by the habit of the embryo. Nevertheless, we discovered that habit could be controlled in part by the orientation of the crystal in the host bath. If a large *a* face were desired, that face was kept horizontal in the solution; and if a large *b* faced crystal were sought, that face or position was made horizontal. No attempt was made to develop a large *c* face, but it is doubtful that any degree of positional maneuvering would be adequate to induce the development of that face.

The ultimate shape of crystalline unit desired was a cylinder for the early masers. Since the hardness of the crystals is about 3.5, they could easily be cut to the desired shape if the proper *a* or *b* face were adequately developed at the onset. The use of a simple power jigsaw or hand jigsaw proved adequate for cutting the crystals. As a matter of interest, however, relative to the shape of the finished crystal, it was decided to grow the crystals to the size and shape desired directly. An *a* faced or *b* faced crystal of about 2 cm. maximum dimension was placed in a cylindrical form and into a host solution. The crystal grew until its maximum dimensions reached 3.5, the inner diameter of the hollow cylinder. The crystal could grow no further in that direction, and further ion accretion took place on the other surfaces until a cylinder 3.5 cm. in diameter and 1 cm. high of the crystalline substance was formed. Some stresses developed in the crystal during this procedure, and flaws appeared, but the crystals thus produced were of fairly good quality.

Due to lack of proper control upon occasion, foreign seeds would grow in random orientation on the desired crystal. These were scraped off while holding the crystals in rubber gloved hands. If the embedding had gone quite far, scraping was difficult, stresses were induced in the crystal, and the quality of the subsequently growing crystal was diminished.

RESULTS OF CRYSTAL GROWING BY REFRIGERATION

Crystals as large as 3.1×4.3×12.5 centimeters were grown in the refrigerator bath. This size is certainly not a maximum; the cutoff at this size was purely a matter of convenience. From the data at hand it appears that the only limitations to size imposed by the method are those mechanical controls such as size of container, size of freezer, and amount of ingredients available. The internal and external quality of the crystals was apparently independent of the size. This may be only apparent, for none of the large crystals was mounted under reflecting goniometric conditions. The quality of the faces of the smaller crystals was not a function of size but, primarily, of the method used in removing the crystal from the bath.

The *rate of growth* of the crystals was dependent upon three primary variables. Obviously, the rate of feeding is important. No attempt was made to attain maximum growth rate, since the quality of the crystals suffers with too rapid growth, and crystals of best quality were desired. The second factor affecting growth rate was the size of the crystal which was growing. All other factors being equal, the larger the crystal receiving ions, the more ions it could pick up. In other words, the absolute growth rate was roughly proportional to size of the crystal. The ratio of growth increment to weight of the host crystal, the percentage growth rate, was inversely proportional to crystal weight. Small crystals grew much faster, percentage-wise than did the large ones. Miss Irita Vilks made a detailed analysis of growth rates relative to crystal size, and this study will appear later. The third factor affecting rate of growth was the habit of the growing crystal. There was a marked slowdown in growth rate for prismatic crystals and *b* faced crystals as compared with *a* faced crystals. No precision measurements were made on this factor, however.

CRYSTAL HABIT

The habit which developed was usually one of three simple types, with {100}, {010}, or {110} predominant, respectively. Figure 1 (left) shows two {100} crystals grown by the refrigeration methods. Figure 1 (right)

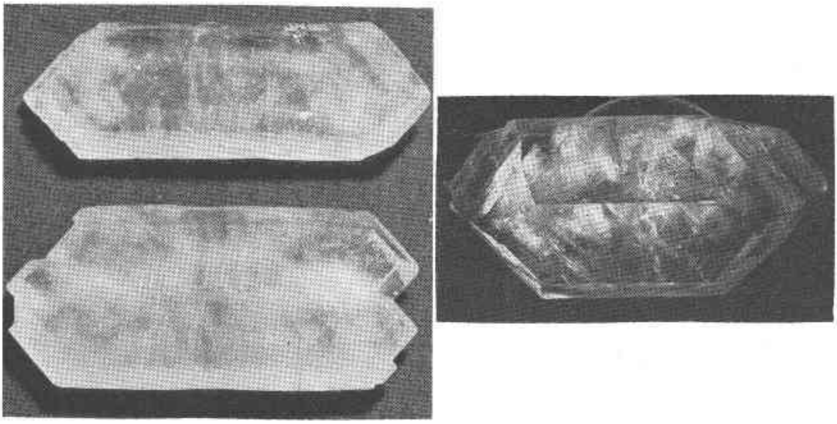

FIG. 1. Crystals of $K_3(Co_{0.995}Cr_{0.005})(CN)_6$.

Left: Elongated parallel to [001] and flattened on {100}. {110} and {111} are modifying forms. (About 8 cm. long.)

Right: Crystal with {110} habit, sitting on pedestal. (About 4 cm. long.)

shows a {110} crystal grown in a 35° C. bath. Three factors were most important in controlling crystal habit. The first of these was the habit of the initial seed chosen as the nucleus for growth and the habit or habits of adjacent growing crystals. The second factor was the orientation of the seed in the bath. No absolute measurements have yet been made concerning the effectiveness of orientation on crystal habit, but qualitative results indicate a significant influence for this factor. The third factor which influenced crystal habit was the composition of the feeding solution. Two variables in this composition occurred. The first was intentional and involved variation in the percentage of potassium chromi-cyanide introduced into the stock solution. Other factors being equal, a higher chrome content in the solutions was generally more favorable to either *m* faced or *b* faced crystals. By proper choice of the initial seed habit, this effect could be minimized. Another compositional variable was accidentally introduced. In the process of adding fresh stock solution to the host bath, some of the old simply saturated solution of the host bath was removed. This was allowed to stand in containers and to evaporate to saturation at room temperature. If this solution were then used as stock solution for later feeding, the growth habit usually became *m* faced. The explanation for this shift lies in the fact that the potassium chromi-cyanide is far less stable than the potassium cobalti-cyanide and hydrolyzes with time. This was in part circumvented by the introduction of potassium cyanide into the solution, but hydrolysis did take place, and the chromium product deriving therefrom was not in an accruable form in the crystal growth. Another serious effect of this process was that the composition of the growing crystal was not the same as that of the original solution, and the saving of the extracted solution from the host containers was discontinued.

The Unit Cell

The unit cell has been measured and reconciled with the morphology. Two polymorphic forms may exist, and the entire subject of unit cell and morphology will be treated in a later paper. It can be stated here, however, that notable deviation from the pseudo-orthorhombic symmetry usually ascribed to the substance is characteristic of the low temperature form.

Quality of Crystals

The effect of rate of growth on the crystals has been mentioned above. The two other primary factors affecting the quality of the crystals were the degree of temperature variation and the amount of mechanical handling required when undesired seeding took place. The temperature variable induced by lifting the trays of beakers from the chest occasionally to permit turning and examination of the crystals for non-oriented seeds was apparently of little influence on the crystal quality. If, however, the crystals were handled, particularly without gloves, differential thermal expansion did induce fractures and other imperfections. The use of gloves partially obviated this difficulty. The mechanical scraping of unwanted seeds from the growing crystals also induced fractures and imperfections, both as a result of the mechanical forces involved in the scraping and because of the temperature variable induced in the handling. The general quality, however, was a transparent slightly greenish yellow excellent crystal. The crystals which contained higher percentages of chromium were deeper yellow in color, less transparent, and generally of poorer quality than the lower percentage crystals.

Successful Use in a Maser

Masers which used the above crystals as amplifying devices were successfully constructed at Lincoln and at Ewen Knight. A microwave signal was successfully beamed at Venus and reflected and picked up at Lincoln Laboratories, using one of the potassium cobalti-cyanide crystals with the slight doping percentage of the chromi-bearing salt. It might be pointed out that early predictions by N. Bloembergen (1956) that such a device would operate with a very low noise factor were completely born out by this experiment.

Limitations of the Technique of Crystal Growth by Refrigeration

One of the outstanding limitations of the technique lies in the difficulty of automatic feeding or automation in general. Any feed line from outside the refrigerator to the container carrying the growing crystal automatically must pass through a cooling zone in which precipitation takes place in the feed tube, finally clogging it and bringing the automatic feeding to a standstill. The fact that the crystals should be periodically turned to make them as perfect as possible also is a limitation to automation. The occasional cleaning of crystals where unwanted seeds have lodged upon them requires a periodic examination. When hundreds of crystals are being grown simultaneously, as in the Ewen Knight Facility, the full-time attention of an operator is required to produce satisfactory results.

The method is, of course, not universal in its application. There must be a significant but not too great a solubility variation with temperature. It is, therefore, necessary to have a fairly rigorous picture of the solubility curve for the substance being grown in order to get the proper differential between the number of ions in solution outside the refrigerator as compared with the saturation conditions in the refrigerator.

The attainment of this goal is particularly difficult if the solubility curve is very steep. Substances with particularly high solubilities do not respond very readily to crystallization by refrigeration. Crystals in which the unit cell has one notably shorter direction, that is, crystals which normally develop an extremely elongated habit, cannot be grown very satisfactorily by the method, although continued study is being made of this variable.

REFERENCE

BLOEMBERGEN, N. (1956), *Phys. Rev.* **104,** 324.

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