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## Crystal Growth in Gels

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*Abstract.* The paper gives a survey of crystal growth in gels, in its historical, technical and scientific aspects. It outlines the various methods now in use and summarizes present knowledge of the nucleation and growth mechanisms involved. The low temperature is specially applicable to crystals which have so far resisted growth by orthodox procedures. It can yield crystals of high optical perfection and is believed to hold a substantial promise of future development.

### 1. Introduction

It has long been appreciated that advances in solid state science depend critically on the availability of single crystal specimens. As a result, an enormous amount of labor and care has been lavished on the development of growth techniques. In terms of size, purity and perfection, the achievements of the modern crystal grower are remarkable indeed, and vast sections of industry now depend on his products. So do the research workers whose preoccupation is with new materials, no matter whether these are under investigation for practical reasons or because a knowledge of their properties might throw new light on our understanding of solids in general.

In one way or another, a very large number of new materials has already been grown as single crystals in recent years, some with relative ease, others only after long and painstaking research. Nevertheless, there are still many substances which have defied the whole array of modern techniques and which, accordingly, have never been seen in single crystal form. Others, though grown by conventional methods, have never been obtained in the required size or degree of perfection. All these constitute a challenge and an opportunity, not only for the professional crystal grower but, as it happens, also to the talented amateur. New and unusual methods of growing crystals are therefore of wide interest and if the crystals are by themselves beautiful, as they so often are, there is no reason why this interest should be confined to professional scientists.

The art and science of growing crystals in gels, largely dormant during the 1930-1960 period and now in the midst of a general renaissance, enjoyed a long period of vogue beginning close to the end of the last century and lasting well into the 1920's. During most of this time, the center of interest was held by the phenomenon of 'Liesegang Rings'. LIESEGANG was a colloid chemist and a photographer who experimented with chemical reactions in gels [1, 2]. He covered a glass plate with a layer of gelatin impregnated with potassium chromate, and placed on it a small drop of silver

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nitrate. As a result, silver chromate was precipitated in the form of a series of concentric rings, well developed and with regularly varying spacings. The discontinuous nature of the precipitation, its geometrical features and the conditions of its occurrence at once became the object of intense, if not altogether successful, investigations. The matter immediately attracted the attention of the great German chemist OSTWALD [3] and, in due course, need one mention it, of Lord RAYLEIGH [4], thereby receiving what must have appeared as the ultimate seal of respectability. The rings were considered interesting, partly because their origin was obscure and partly because they were reminiscent of certain structures found in nature, e.g. the striations of agate. Often they consisted of apparently amorphous material. In due course, the achievement of microcrystalline reaction products also became desirable, because of the ease with which they could be identified by means of  $x$ -ray photographs. Larger crystals, e.g. of several mm size, were occasionally obtained but not systematically looked for. In contrast, the growth of such crystals is the principal objective of all modern work in this field. An early claim by FISHER and SIMONS [5] to the effect that 'gels form excellent media for the growth of crystals of almost any substance under absolutely controllable conditions' survives as a shining example of faith, only slightly tarnished by the sporadic nature of its fulfillment to date.

Surprisingly, in view of the history of this subject, the Liesegang Ring phenomenon itself is even now only imperfectly understood. It has been displaced from the center of interest and still awaits the talents of a modern OSTWALD, with an appreciation of its beauties and with a great deal of time to spare. There is no basic mystery, in the sense that periodic solutions of the diffusion equations (with appropriately chosen boundary conditions) are known to exist in principle, but little is known about the parameters involved and nobody has succeeded in relating theory to practice. Periodic ring and layer formations found in nature offer only the most limited opportunities for research into their origin. Indeed, many are due to very different mechanisms. As one critical analyst has put it when faced with the suggestion that the stripes on tigers and zebras may be glorified LIESEGANG phenomena: 'enthusiasm has been carried beyond the bounds of prudence', [6] a verdict with which the present writer is inclined to concur.

The experiments during the early period derived a good deal of impetus from the interests of geologists, in the belief that all quartz on earth was at one time a silica hydrogel. A vein of white gelatinous silica, as yet unhardened by dehydration, was indeed reported to have been found in the course of deep excavations for the Simplon tunnel [7]. Moreover, some early experiments were on record (quoted by EITEL [8]), according to which microscopic silica crystals had been obtained from silica gels in the presence of various 'crystallizing agents' when heated under water vapor pressure. Quite plausibly, then, crystalline foreign deposits found in quartz may be examples of crystal growth in gel. In this way, the gel method appeared to offer systems and opportunities for experiments in 'instant geology' [9]. Figure 1 shows typical examples of natural growth, needles of tourmaline in single crystal quartz. It is obvious that the needles must have grown first, but current opinion among geologists and mineralogists no longer favors the idea that single crystal quartz is derived from a gel, it being thought more likely now that this particular form is the outcome of hydrothermal growth. Little is known about the viscosity of the hydrothermal medium under the

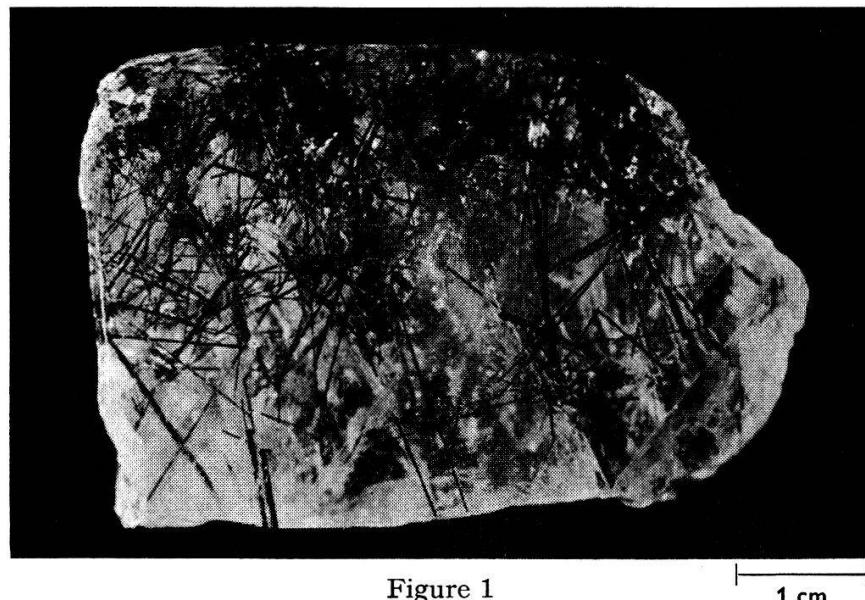


Figure 1  
Tourmaline in quartz.

original growth conditions, but it is plausible to suppose that the tourmaline and rutile needles grew in such a medium when it was fluid but viscous. This belief is supported by the knowledge that a gel as such, though generally beneficial, is not absolutely required for the mode of crystal growth here under discussion. On the general subject of the role of gels in geology, there is an extensive early literature [10, 11]. In the last analysis, the problem of consistency is not yet unequivocally settled as far as quartz is concerned, but there are many examples of crystal growth in other viscous media. Among the unwelcome manifestations of the process are the occasional growth of ice crystals in ice cream, the growth of tartrate crystals in cheese, the crystallization of sulphur in rubber [12], the growth of zinc salts in dry batteries, and, in rapidly descending order of desirability, the growth of uric acid crystals in joints and of stones in human organs. The subject thus has much wider implications than is generally believed, *inter alia* because it is distantly related to our understanding of the processes which take place in photographic emulsions.

## 2. Work During the Early Period

In the course of early work (e.g. up to 1930) a mass of empirical data was assembled, much of it too imprecise and unsystematic to lead to any real insight into the mechanism of the phenomena involved. However, some of these investigations remain interesting because they have the character of 'existence theorems', illustrating at least some of the things that can be done and suggesting new lines of experimentation.

Among the indefatigable enthusiasts was HATSCHEK [13], working primarily with (5–20%) gelatin and (1–5%) agar gels. He was the first to make a systematic study of particle size distribution in a great variety of Liesegang Rings. Amongst other things, he noted that in ring systems prepared by allowing sodium carbonate to diffuse into a gel charged with barium chloride, distinct and well-formed  $\text{BaCO}_3$  crystals of up to 1.5 mm length are occasionally found in the otherwise clear space between adjacent rings. The observation must have been the first hint, if one was

needed, that Liesegang Ring formation is indeed a complicated process, especially since OSTWALD and MORSE and PIERCE [14] had earlier set great store by the sharpness with which the rings are often defined. Moreover, it has since been amply demonstrated that Liesegang Rings themselves may consist of substantial crystals, e.g. as shown in Figure 2. Silver dichromate, and the dichromate, chromate, chloride, iodide and sulphate of lead, as well as calcium sulphate and barium silicofluoride were included in HATSCHÉK's crystal growing repertoire. He was also the first to report that crystals grow generally better in silicic acid gels than in gelatin or agar. In one of the most truly interdisciplinary experiments on record, MARRIAGE [15] had earlier grown lead iodide crystals in fruit jellies and jams.

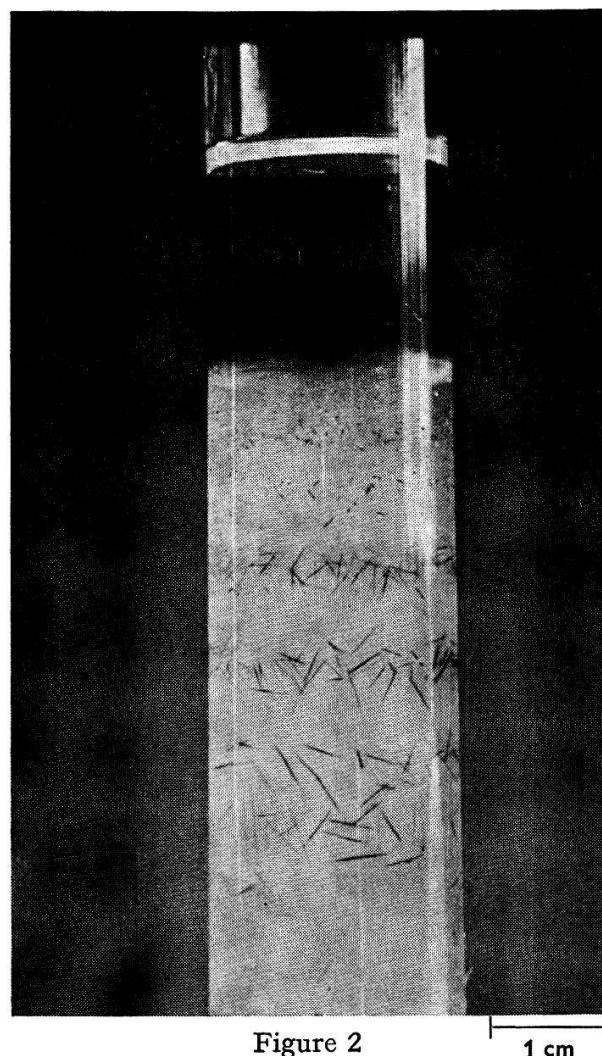


Figure 2  
Silver chromate crystals in Liesegang Rings.

It was always realized that reagents could be diffused into a gel, and conversely, that gels could be dialized to free them of excess reagents or unwanted reaction products. Such experiments were conducted by HOLMES [16] who used the dializing process for the treatment of gels in U-tubes, in order to eliminate excess reagents which might interfere with the two diffusing components. HOLMES also grew single crystals of copper and gold by diffusing a reducing agent into gels charged with the respective salts. HATSCHÉK had done so before, but HOLMES claimed 'better results than any yet

recorded', without actually mentioning crystal sizes. Both experimenters concerned themselves to some extent with the effect of non-reagent additives such as glucose, urea and gum tragacanth on crystal growth. HOLMES and also DAVIES [17] noted that reactions in gels can occasionally be influenced by light and, in particular, by short wavelength ultraviolet radiation. HOLMES used alkaline gels for the formation of cuprous oxide, but the product was always amorphous.

One of the most important early experiments was carried out by DREAPER [18] who wanted to elucidate the role played by the capillarity of the gel structure. For this purpose, he substituted fine sand and even a single capillary tube for the usual gels and found that crystalline growth products could be obtained with such systems. HOLMES later used barium sulphate and alundum powders for the same type of demonstration. Strictly speaking, these experiments prove nothing in particular about the nature of gels, but they serve as a valuable hint of the circumstances which favor single crystal formation. A comprehensive survey of early work on gel structures has been given by LLOYD [19]. Structure and classification problems were hotly debated by scientific workers in the 1920's and earlier, often with enviable self-confidence and just occasionally with a trace of venom [20].

### 3. Growth Procedures and Mechanism

Growth procedures which would satisfy the chemical production engineer have not yet been developed; meanwhile, laboratory experiments are always on a small scale. The most common procedure is to diffuse a solution of one reagent into a gel containing another, as shown in Figure 3a. If the reaction product is relatively insoluble and does not nucleate excessively, at least some good crystals will generally form in the gel. The archetype is calcium tartrate, made in a sodium metasilicate gel containing tartaric acid by diffusing calcium chloride. The process yields large (e.g. 1 cm) crystals of fine optical quality. Other virtues of this material have revealed themselves only sparingly. Even the keenest aficionados of gel growth will admit that

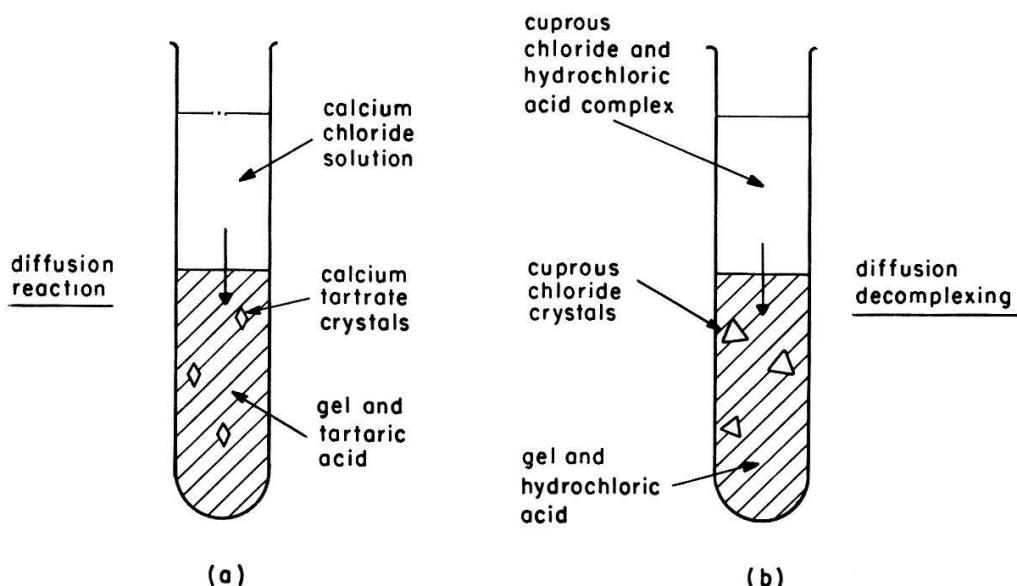


Figure 3  
Typical growth procedures.

calcium tartrate is grown not for its compelling fascination but precisely because it grows so well and thus lends itself to a variety of general studies on the behavior of gel systems. For best results, certain procedural recommendations should be followed [21], but the process remains essentially simple. By diffusing a reducing agent into a gel containing a metal salt, a similar procedure can be used to grow metallic crystals, e.g. of copper and gold. As far as is known, alloys have not yet been produced; an attempt in that direction may well be interesting and rewarding.

In all cases explored so far, silica gels have proved most successful, and growth temperatures in the neighborhood of 45°C more favorable than room temperature. By changing chemicals in mid-reaction, it is possible to form heterojunctions in selected cases and, by adding small amounts of other substances, the crystals can be doped. Indeed, they can be made to accept a surprisingly high percentage of incompatible dopants while remaining outwardly clear and orderly. When deformed, e.g. by gentle touching with a glass rod, they shatter instantly and audibly, thereby releasing the internal strain. The ease with which 'overdoping' can occur may have something to do with the yielding nature of the gel which, in a sense, serves as a three-dimensional quartz 'crucible' but exerts only very small constraining forces on the growing crystal. Since the silica network is chemically stable, it does not itself contaminate the growing crystals to any appreciable extent. Indeed, the silicon contents of the best crystals are in the region of a few parts per million, a remarkable purity in the circumstances.

With all convection currents thoroughly suppressed, there is no doubt that the crystals grow by diffusion. On the basis of FRANK's theory [22] and if one accepts the spherical model (crystal radius  $R$ ) on which it is based, this should lead to a growth law such that  $R^2$  is proportional to time. This has been confirmed, at least to the level of accuracy that might be expected from the approximations made [23]. The square law relationship can prevail only during an intermediate growth period, after the establishment of steady-state conditions and before exhaustion of the solute reservoir. In due course, growth ceases for two principal reasons: because the available reagents have been used up [24] and because the crystals are increasingly soluble in the waste products of the reaction. When this happens depends, of course, on the initial reagent concentrations used, on the distances between nearest neighbors and, to some extent, on the size of the container. In an attempt to encourage continued growth, it would certainly be possible to replenish the original reagents (e.g. using a U-tube instead of the system on Figure 3a), but ultimately this can be successful only if the waste products of the reaction are also removed. In principle, this could be done by repeated dialyzing of the gel, but the process is then neither fast nor simple. Alternatively, it is possible to re-seed a crystal into a new gel [25], once or repeatedly, and thereby to increase its size by a substantial factor. After each re-implantation, the temperature must be temporarily raised in order to dissolve the (usually damaged) surface layers of the seed.

There are other ways in which the gel system can be used. Certain desirable crystal materials can be diffused into a gel (uncharged with reagents) in complexed form, and allowed to de-complex with increasing dilution. ARMINGTON and O'CONNOR [26] have used this principle for the growth of CuCl, originally complexed with HCl (Fig. 3b). In a similar way, HALBERSTADT [27] has grown AgI from a complex with KI as

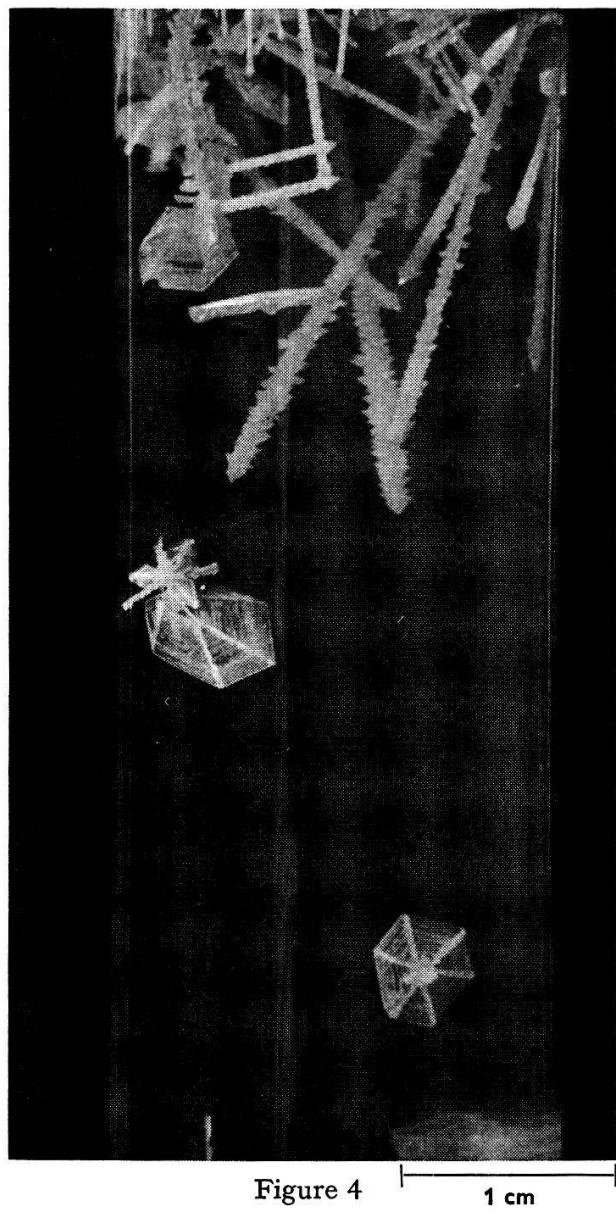


Figure 4  
Gel-grown AgI crystals.

shown in Figure 4. It may also be possible to grow crystals which are soluble in (say) acid by diffusing the solution into an alkaline (or, perhaps, merely less acid) medium. Another way would be to charge a gel with the dissolved material to be grown and to nucleate crystals simply by cooling. This is, of course, very similar to growth from solution, except for the advantages in connection with nucleation control (see below) which arise from the presence of the gel.

#### 4. Nucleation, Size and Perfection

It has been amply demonstrated that the gel method is capable of yielding crystals of substantial size and a very high degree of optical perfection. Whether it actually does so in any particular case depends on circumstances. Since the crystals in any one system compete with one another for solute, their ultimate size is directly related to the nucleation probability. Nucleation is thus one of the key issues, and the extent to which nucleation can be controlled will ultimately govern the practical utility of the

gel technique as a whole. The suppression of nucleation is, indeed, believed to be the principal function of the gel.

As in solution, it is possible to envisage homogeneous and heterogeneous nucleation mechanisms. That heterogeneous nucleation takes place cannot be in doubt; a simple comparative experiment using unfiltered tap water instead of the distilled or de-mineralized variety demonstrates that the number of growing crystals is much increased. In some cases, the presence of foreign nuclei has been directly demonstrated by local analysis, using an electron probe [28]. At the same time, experiments with artificially introduced nucleation centers have shown that the gel allows only a few of the potentially active nuclei to function efficiently. The remainder are presumably immobilized, either by being tightly surrounded by gel silica or else by finding themselves in cells which contain insufficient solute to lead to the formation of a macroscopic crystal. It is reasonable to suppose that the gel deals in the same way with foreign nuclei originally and accidentally present.

By a variety of arguments, one can similarly persuade oneself that not all the crystals formed owe their origin to the presence of foreign substrates, and that a certain amount of homogeneous nucleation must be possible. This follows, for instance, from observations on the smallest gel-grown  $\text{PbI}_2$  crystals which are entirely free from dislocations. It is also in harmony with the results of experiments on pre-saturation [21]. Interesting as this conclusion is, it limits the steps which can be taken with a view to achieving nucleation control beyond that exercised by the gel automatically. On the other hand, such possibilities as remain have not yet been exhausted. One successfully used [25] involves concentration programming of one of the reagents, to ensure that the concentration gradients are low when nucleation takes place and higher later during growth. Another possibility is to search for gels with a 'suitable' cell size distribution. This is, presumably, one in which all but a few of the cells are too small or insufficiently communicated with others to support macroscopic growth. There are indications that gel age is a factor in promoting desirable situations of this kind, probably as a result of the continued formation of cross-linkages. The task is, of course, to find a suitable system and procedure which suppresses nucleation without leading to increased contamination, a danger which arises especially when nucleation is influenced by means of reagent additives. It has been shown, for instance, that ferric ions promote the nucleation of calcium tartrate crystals when present in small concentrations (a few ppm), but suppress it in larger concentrations. The increased iron content of the large crystals then obtained is a penalty of this suppression. One of the most potent methods of nucleation control (and perhaps *the* most important) is the adjustment of pH or, more generally, of any other parameter which increases the solubility of nuclei and thus diminishes the probability of their large-scale survival [21].

Gel systems can vary enormously in character and appearance but one feature appears to be common to them all: the best crystals grow at considerable depths below the diffusion interface, where they nucleate only sparingly. A variety of *ad hoc* explanations can be devised [21] and all are probably valid in varying degree, but the most widely applicable is that which connects the comparative rarity of nuclei with the arrival rate of solute in the concentration gradient. When that gradient is high, as it is near the diffusion interface, the arrival rate is also high and the nuclei formed are likely to be imperfect (non-classical). The converse would be true at greater depths.

Since the degree of perfection affects the energy content and thereby the formation probability of a critical nucleus [29], a plausible connection between position and perfection is readily available. It may be possible to exploit it for the growth of larger and better crystals.

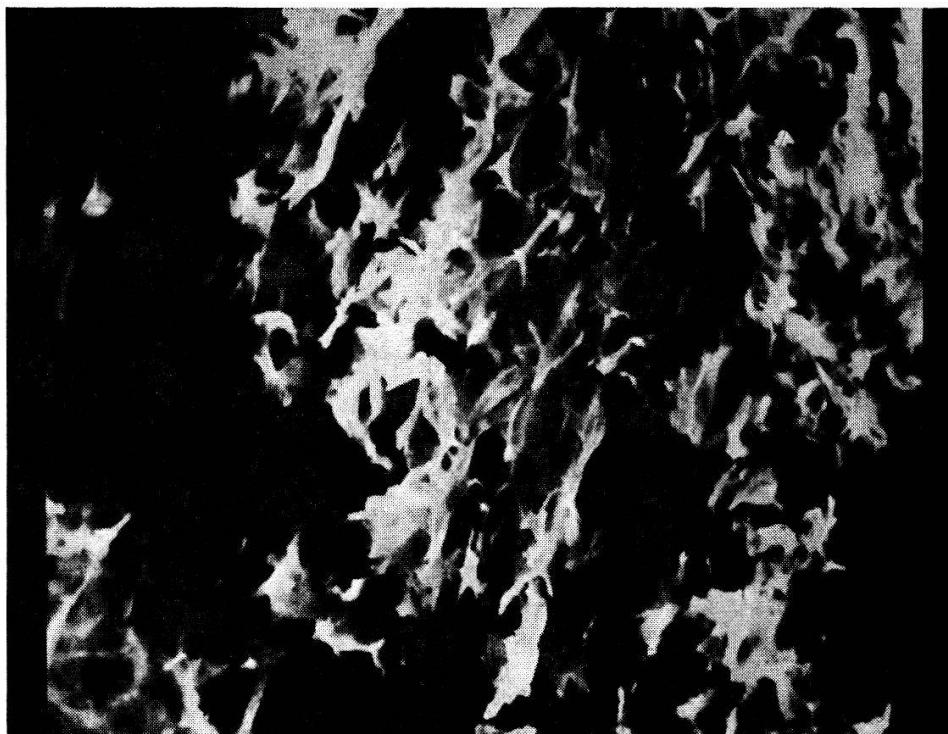


Figure 5

Scanning electron-microscope picture of quick-frozen vacuum dried gel.

There is little doubt that the most undesirable feature associated with crystal growth in gels is the gel. Being neither solid nor liquid, it lends itself to very little precise investigation, at any rate in the form in which it is actually used. So it comes that we know precious little about the microscopic and sub-microscopic structure of hydrogels and about the manner in which this structure affects crystal nucleation and growth. Additional problems arise from the difficulty of distinguishing primary and secondary mechanisms. For instance, fewer (and hence better) crystals may grow in gels of smaller average cell size, but it has not yet been incontrovertibly established whether this is due to the smaller number of suitable nucleation sites in such media or due to a slowing down of diffusion (see above). Quite recently, a method of investigation has been devised which is showing a good deal of promise [30]. Gel specimens are repeatedly washed with distilled water to remove all solute, then quickly frozen at liquid N<sub>2</sub> temperatures and placed into a vacuum. During this process, the water (ice) is removed, and since there is no visible shrinkage during evaporation, it is reasonable to assume that the three-dimensional hollow gel structure remains intact. It is then shadowed with an evaporated gold layer and inspected under a scanning electron microscope. Figure 5 shows a typical result. Although the structure is not simple, it should be possible to 'characterize' hydrogels in this way and to study the manner in which gel structure and nucleation probably are related.

### 5. Hopes and Aspirations

In the vast repertoire of methods which the modern crystal grower has at his disposal, growth in gels is surely the most neglected item. Yet the procedure has shown itself remarkably versatile and capable of producing, at room temperature or close to it, crystals with a remarkable degree of perfection. Because it depends essentially on the suppression of nucleation, its use or, at any rate, attempted use, makes good sense for a variety of materials. Metallic crystals, oxides, laser hosts, etc., may be grown in this way, and the possibilities for growing difficult organic crystals have scarcely been touched upon. There is, moreover, every reason to believe that the method is now only at the beginning of its development. A small monograph on its history and present status is in preparation [31].

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