INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/382- 3

WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"Crystal Growth from Water Solution on Ground and in Space"

"Diagnostic Methods to Study Crystal Growth from Transparent Solution"

F. BEDARIDA
Dipartimento delle Scienze della Terra
Sezione di Mineralogia
Università di Genova
Genova, Italy

Please note: These are preliminary notes intended for internal distribution only.

CRYSTAL GROWTH FROM WATER SOLUTION ON GROUND AND IN SPACE.

Federico Bedarida - Dipartimento di Scienze della Terra
Sez. di Mineralogia - Università. C.Europa 26 16132 Genova Italy

SUMMARY

Crystal growth from solution is the crystallization of a compound that is very different from that of the initial liquid phase. The most common solvents are water, multicomponent aqueous or non aqueous solutions and melts of some chemical compounds.

Crystal growth from solution is one of the commonest way of growing crystals and the commonest solvent is water. The importance of water does not need to be pointed out, but some anomalies have to be taken into account. The point is that the properties of water do not vary in a constant way with temperature, as it was yet controlled by Miers and Isaac at the beginning of the century.

The apparatus for these experiments is generally rather simple, the crystals may grow sometimes with a good perfection and one can play in a wide range of growth temperature conditions, composition of the medium and types of impurities if necessary.

Since the crystal may grow at temperatures far below their melting points, they generally have a higher perfection than those grown from the melt. On the other hand the presence of the solvent materially affects the kinetics and the mechanism of growth.

As far as there is migration of the nutrient on crystal faces, diffusion plays an important role. So two types of diffusion are always considered: surface diffusion and volume diffusion. Volume diffusion coefficients may be accurately measured with holographic interferometry, as it will be illustrated in the second lecture.

Since in crystals the faces are of different structural types (F,S,K) also this point would be considered in an accurate work. The emergence of a dislocation on a face will also have its importance.

The reactions at the crystal-solution interface are complicated by the adsorption on the growing surface and by the interaction between the particles of the crystallizing substance and the solvent (hydration in aqueous solution and solvation in non aqueous ones).

The subject is too much complicated to be easily put in theoretical terms, so that one can better find pragmatic descriptions in place of uncertain theoretical ones.

Some schematic examples of types of interface will be given.

Let us now suppose to introduce a solid in water, better of course if it is soluble! If this is the case the water molecules and the "particles" of the solute are in a continuous movement. Some solid "particles" leave the surface and go into the liquid, in the same time some "particles" of the solute are deposited on the solid. There is equilibrium when the two flows are equal. The number of "particles" captured by the solid is proportional to the number of shocks on the surface; one can admit that the liquid to solid flow is proportional to the dissolved particles. On the contrary the flow coming out from the solid depends only on temperature and pressure values, and the concentration of the solution is not so strong in general to have an influence. The equilibrium will be reached at a value of the concentration for a given substance depending on temperature and pressure. This is called "solubility limit". Beyond the solubility limit there is supersaturation whose degree is essential for crystal growth.

The phenomenon is not of course so simple as in this description. Let us take for istance ionic crystals in solution. The ions do not move "naked" in the solution. Since they have an electric charge they produce a field, the electric dipoles of the water molecules are attracted and around the ion a shell is built. For this reason the ions of different sign protected by this shell of water molecules cannot much easily come enough close. For this reason they will remain dispersed in water unless a sufficient degree of supersaturation will allow them to overcome the energy barrier and they, losing their shell will stick to the surface of the crystal.

This is the physical meaning of solvation and desolvation that were introduced before.

A further complication is that the structure of the solvated ions is not generally well defined. But this is not the task of this lecture.

So far for a general information.

But why growing crystals from solution in space? The principal reason to experiment crystal growth from solution in space is to avoid convection. Convection generates many types of defects in the crystal such as dislocations, impurity segregations and compositional inhomogeneities. But to grow crystals from water solution one must further keep in mind some peculiar properties of water as told in the beginning, since the presence of the solvent has always a physical influence on the process of growth of the solute crystals.

Gravity is the main cause for convection. When the crystal grows, two effects may join their influence. The nutrient solution around the crystal has become less concentrated and lighter and goes up, the heat of crystallization cooperates to the phenomenon (even if sometimes at a negligible extent). The microgravity environment, keeping out convection, therefore enables to achieve diffusion-controlled growth. There are however different sources of convection related to the growth process itself and the Marangoni effect whenever there are free liquid surfaces or bubbles present.

These effects may become dominant and careful hydrodynamic studies of heat and mass transfers are a prerequisite to the space experiment.

One beam holographic interferometry control (as in the German space instrument Holop) and more sophisticated methods will give a fundamental information (second lecture).

A list of the experiments of the past years made by Americans, Europeans and Soviet groups will be given.

The main results have been crystals with higher perfection than those grown on earth with far less striations and fewer dislocations.

Real time holographic interferometry proved that growth in space is only dependent on purely diffusion controlled conditions and since the quality of the crystals obtained is better, this proves that convection is one of the main causes for defects. Multidirectional holographic interferometry will give even better results as far as a map of the concentration around the crystal is required.

In experiments on ground, crystals may be grown with a pure diffusive process only if they grow in gel and this may be a condition for previous experiments and simulations on ground. The gel plays two roles in the growth of crystals: first it allows the mass transfer to be governed by diffusion so that this transfer can be thoroughly regulated even at a very small rate on a microscopic scale; and second it mantains the growing crystal at its nucleation site since the crystal cannot sediment and it may therefore grow in all directions.

But there is a drawback: the crystal may be contaminated by gel inclusion from which dislocations bundles may propagate in every growth sector.

Anyway, after the results reached in the first experiments some practical suggestions have been given for the growth of crystals from solution in space. New diffusion experiments aimed to crystal growth have to be done along with precise measurements of actual values of diffusion coefficients. Also the distribution in real time of the gravity levels have to be taken into account. Programs for fundamental research on crystal growth from solution in space in a pure diffusive environment should be proposed. The programs for making experiments in space usually have been extrapolated from experiments on ground. It is reasonable that in the future new and original criteria should be applied in microgravity since the proofs on ground not only may be useless, but they could be even misleading.

REFERENCES

A.A.CHERNOV
Modern Crystallography III (Crystal Growth) - Springer Verlag (1984) 353-414

J.W.MULLIN
Crystallization - Butterworths (1972) 165-166,252

J.C.BRICE
The growth of crystals from liquids - North Holland Publishing Company (1973) 8-10, 78-127

H.U.WALTER (editor)
Fluid Sciences and Materials Science in Space - Springer Verlag (1987) 404-449

DIAGNOSTIC METHODS TO STUDY CRYSTAL GROWTH FROM TRANSPARENT SOLUTION

Federico Bedarida - Dipartimento di Scienze della Terra
Sez. di Mineralogia - Università. C.Europa 26 16132 Genova Italy

The subject of this lecture deals with applications of holography in crystal growth from transparent solutions.

Holography has been discovered by Dennis Gabor in 1948 and is an interference phenomenon between waves. The waves may be in theory of any type: sound, X rays, corpuscolar waves, light. The most valuable results have been achieved with coherent light.

In this lecture the results obtained in the application to crystal growth from solution will be discussed along with the perspectives of this type of work.

The word holography has the Greek root "olos" that means the whole and probably Gabor intended that both informations on amplitude and phase are given.

The normal photograph is a two dimensional projection of the object, described by the distribution of the square of the amplitude $A^2=I$.

The hologram on the contrary reconstructs the wave field reflected by an object.

But even if the discovery of Gabor was done in 1948, the first holograms were obtained only in 1963 by E.Leith and J.Upatnieks using the light of a laser. At that time Dennis Gabor sustained that he had almost forgiven holography.

Holography is then a way to reconstruct tha wave field diffused by an object. A step forward is holographic interferometry, a method to check the interference between two registered wavefronts, or one registered wavefront from an object.

To day the method is largerly used to measure:

1) surface displacements of opaque objects, and
2) refractive index variations of transparent objects.

Both these informations may be used for crystal growth, but in this lecture I shall deal mainly with the second.

The first applications of holographic methods in the laboratory of the University of Genoa were used to check microtopography of surfaces of crystals as grown: their effectiveness is good and their application is easy.

The second applications have been to study crystal growth from solution.

Interferometry with thermal light has been used since many years to study crystal growth from solution along with the changes of concentration of the solution.

Only in these last ten or fifteen years laser light has allowed to improve the experiments as a consequence of the coherence of its light, offering the possibility of studying much larger volumes. For this reason new holographic interferometric methods have been devised. Two of them will be discussed in this lecture.

First method - one beam interferometry,

The scheme of the experimental apparatus is given in the drawing (fig.1). Two collimated laser beams obtained through the variable beam splitter are reflected by the mirrors and are spread by the objective and the lenses. The first beam, object beam, crosses the solution where nothing happens and interferes with the second, referance beam, on the holographic plate. The plate after exposure is developed and then replaced exactly in the same position and enlightened with the reference beam. The reconstructed wavefront registered by the hologram can interfere

with the wavefront that has crossed the solution. If the plate is in the exact position and nothing has happened to the solution, no fringe will be seen. If the concentration of the solution is changing, interference fringes are formed which show how much the optical path is changing.

An apparatus qualified for space, based on the same principles, has been prepared by DFVLR, it is called Holop and has yet been flawn.

The progress of the experiment of growth can be followed in real time and simultaneously registered using a TV camera, a monitor and a TV recorder. Sodium chlorate was chosen in the beginning as a model crystal, since in aqueous solution it has a broad metastable region under supersaturated conditions and well shaped single crystals may grow from a seed without simultaneous precipitation of many tiny crystals. A thermostatic cell was used. The supersaturation desired was achieved lowering the temperature. From the fringes shown in fig.2 it is possible to deduce the movements that take place in the solution during the process of growth. The crystals studied have been sodium chlorate, sucrose and the mineral epsomite.

The importance of the method relies on the fact that an experiment can be followed in real time, and detailed results will be shown. On sucrose crystals for istance it has been possible to control how the diffusion boundary layer varies from face to face of a single crystal and how the distribution of captured impurities on a given crystal face can influence the isoconcentration curves and hence the variation of the boundary layer in time and position over the face.

The drawback of the method but not critical at all, is that only semiquantitative information can be deduced by the phenomenon under study.

Second method - Multidirectional holographic interferometry

A premise has to be given. The problem that deals with multidirectional holographic interferometry is a very general one in physics and is the problem of the image reconstruction from projections. With the word image is meant a distribution of a physical property in the three dimensions. With this, meaning that the word image is used to represent some property of an object or physical system: in our case the measurement of a variable concentration.

It is well known that in medicine computed X-ray tomography and more recently NMR (nuclear magnetic resonance) are very probably the most significative applications up to this moment of image reconstruction from projections, whose mathematical principles were firstly settled by Radon.

An outstanding point of these techniques is that non invasive examination is used.

Multidirectional holographic interferometry based on the same principles has the important advantage of being not invasive and may be called optical tomography.

An optical scheme of the simplified apparatus is given in fig.3.

The concentration field in the neighborhood of a crystal growing from a supersaturated solution can be reconstructed by this method. Simultaneous interferometric images are obtained in different directions: the total angle of view is limited by the geometry of the experimental apparatus.

Each interferometric image corresponds to he projection of the three-dimensional refractive field along a certain direction; by an image elaboration system the digitalized intensity plot at a certain level δ from a crystal face is obtained and the related phase variation is calculated. The numerical inversion of the system of integral equations, previously reduced to a system of linear equations, gives the reconstruction of the refractive

index field in a plane at the distance δ from the crystal face:the concentration field is obtained straightforward iterating the values plane by plane.

The determination of a field from its projections belongs to the class of the ill-posed problems: a method to regularize the inversion has been developed, leading to a good reconstruction that is optimizing some experimental parameters.

By an experimental point of view, a new optical schema has been realized, covering an angle of 115°: in fact, different test functions in a typical simulation procedure have been correctly reconstructed using at least six not equispaced views distributed over such a total angle.

The work is in progress on both sides: to improve the experimental apparatus and to implement the mathematical methods. The techniques just described have many advantages to study crystal growth from solution and they may be applied on earth and in space, even if the second method being much more sophisticated will require some further improvements.

In the main program of these researches a third method using coherent optics, but not based on holography, is now under study. The aim is to enhance the resolution power. The first results will be ready probably at the beginning of summer.

REFERENCES

E.Leith and J.Upatnieks - J.Opt.Soc.Amer. 53, 1377, (1963)

E.Leith and J.Upatnieks - J.Opt.Soc.Amer. 54, 1295, (1964)

D.Gabor - Opt.Spectra, 32, oct. (1970)

F.Bedarida and C.Pontiggia - Acta Crystall., A24, 614, (1968)

F,Bedarida, C.Pontiggia, L.Zefiro - J.Cryst.Growth, 24/25, 327, (1974)

F.Bedarida, C.Pontiggia,L.Zefiro - J.Cryst.Growth, 34, 79, (1976)

F.Bedarida, C.Pontiggia, L.Zefiro - in Applications of holography and optical data processing, ed.E.Marom & A.A.Friesem, Pergamon Press 249, (1977)

D.Aquilano, F.Bedarida, P.Boccacci, G.Mantovani, M.Rubbo, G.Vaccari, L.Zefiro - in Materials under extreme conditions, ed.H.Ahlborn, H.Fredrikson, E.Luscher, Les editions de physique, 33, (1985)

G.T.Herman and R.M.Lewitt - in Topics in Appl.Physics, ed.G.T.Herman Springer, Berlin, 1, (1979)

F.Bedarida, P.Boccacci, L.Zefiro, C.Pontiggia - Phys.Chem.Hydrod. 2,327, (1982)

REFERENCES

E.Leith and J.Upatnieks - J.Opt.Soc.Amer. 53, 1377, (1963)

E.Leith and J.Upatnieks - J.Opt.Soc.Amer. 54, 1295, (1964)

D.Gabor - Opt.Spectra, 32, oct. (1970)

F.Bedarida and C.Pontiggia - Acta Crystall., A24, 614, (1968)

F,Bedarida, C.Pontiggia, L.Zefiro - J.Cryst.Growth, 24/25, 327, (1974)

F.Bedarida, C.Pontiggia,L.Zefiro - J.Cryst.Growth, 34, 79, (1976)

F.Bedarida, C.Pontiggia, L.Zefiro - in Applications of holography and optical data processing, ed.E.Marom & A.A.Friesem, Pergamon Press 249, (1977)

D.Aquilano, F.Bedarida, P.Boccacci, G.Mantovani, M.Rubbo, G.Vaccari, L.Zefiro - in Materials under extreme conditions, ed.H.Ahlborn, H.Fredrikson, E.Luscher, Les editions de physique, 33, (1985)

G.T.Herman and R.M.Lewitt - in Topics in Appl.Physics, ed.G.T.Herman Springer, Berlin, 1, (1979)

F.Bedarida, P.Boccacci, L.Zefiro, C.Pontiggia - Phys.Chem.Hydrod.

F.Bedarida - J.Cryst.Growth, 79, 43, (1986)

F.Bedarida, L.Zefiro, P.Boccacci, C.Pontiggia - in Proc. 4th Europ. Symp. on materials under microgravity, Madrid, 139, (1983)

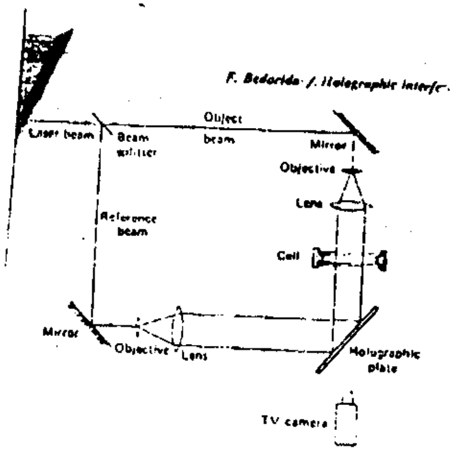

Fig.1. Schematic diagram of the experimental apparatus.

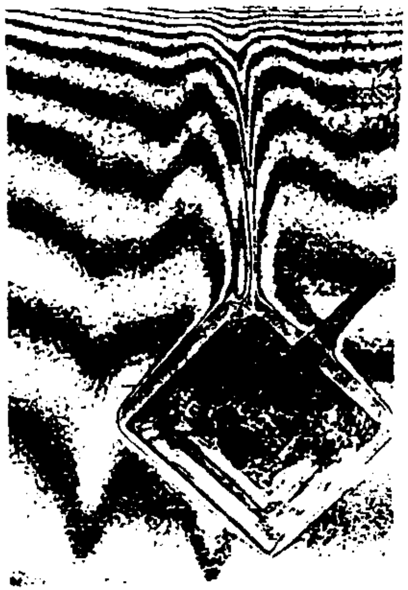

Fig.2. Interferogram of a $NaClO_3$ crystal growing in a solution

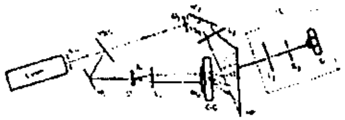

Fig.3. Schematic diagram of the experimental apparatus for multidirectional holographic interferometry: SH = shutter, VBS = variable beam splitter, M = mirror, O = objective, S = spatial filter, L = lens, PG = phase grating, GC = growth cell, HP = holographic plate, C = camera, OS = optical system.