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Biological and Physical Space Research Laboratory 2002 Science Review

P.A. Curreri, M.B. Robinson, and K.L. Murphy, Editors

Marshall Space Flight Center, Alabama

December 2003

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National Aeronautics and
Space Administration

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TECHNICAL MEMORANDUM

BIOLOGICAL AND PHYSICAL SPACE RESEARCH LABORATORY 2002 SCIENCE REVIEW

1. INTRODUCTION

The Biological and Physical Space Research Laboratory resides in the Microgravity Science and Applications Department (MSAD), which is part of the Marshall Space Flight Center (MSFC) Science Directorate. The historical roots of this laboratory reach back more than thirty years. Formally, before Center reorganization in 1999, we were part of the Space Science Laboratory, SSL. This laboratory consisted of a small group of about 100 civil service Ph.D. level scientists. SSL also included equivalent divisions focusing on Space Science, Earth Science, and Space Optics, which are currently located off-site in the National Space Science and Technology Center (NSSTC).

A dedicated science laboratory can have a very powerful positive influence on the productivity of a larger organization such as the Marshall Space Flight Center. Science is the most efficient way we know to obtain new knowledge about nature, and thus is essential for the success of an endeavor without precedence such as the exploration and development of space. An academic research laboratory, by design, diverges into many research directions; an internal laboratory such as ours focuses its science completely on research pertinent to the goals and objectives of its host organization. According to Center lore, the science laboratory was initiated by the need to interact with Dr. Van Allen who had the first science payload (essentially a Geiger counter) on the Army's Redstone Rocket. The experiment resulted in the discovery of the Van Allen Radiation Belts around the Earth. Soon Marshall's science laboratory, with the encouragement of Dr. von Braun, began to work on the concept of a telescope above Earth's atmosphere. This eventually became the Hubble Space Telescope and led to the great observatory programs. After the successful Apollo program was terminated, the Skylab space station was developed with the adaptation of unused Saturn V hardware. To provide science for Skylab, Marshall's science laboratory helped lead the development of an x-ray telescope to study the Sun, which eventually led to Chandra, the highly successful outward looking x-ray telescope in orbit today, and to microgravity materials science, fluids and combustion experiments. This Microgravity Science Program, along with other biological research, led in turn to the highly successful Spacelab series of missions, and became the major science justification for the International Space Station (ISS). It has been estimated that these programs, including the ISS, have generated about one-half of Marshall's program workload over the past 20 years. Thus, the Biological and Physical Space Research Laboratory (and the new Propulsion Research Laboratory) carries on a tradition of MSFC on-site science, begun under the direction of Dr. Werhner von Braun, into the future.

With the International Space Station Program approaching "core complete," our NASA Headquarters sponsor, the new Code U Enterprise, Biological and Physical Research, is shifting its research emphasis from purely fundamental microgravity and biological sciences to "strategic research" aimed at enabling human missions beyond Earth orbit. Although we anticipate supporting microgravity

research on the ISS for some time to come, our laboratory has been vigorously engaged in developing these new strategic research areas.

Within the MSFC organization, the Biological and Physical Space Research Laboratory comprises the science unit of the Microgravity Science and Applications Department. The MSAD is divided into seven groups with a total of about 100 civil servants and a flexible number of associated contractor personnel. In this department, our science group is organized along with planning, systems engineering, project management and operations groups. The science group is composed of about 30 civil servants, of whom more than 25 are Ph.D. level scientists. The laboratory is organized into three disciplines: Materials Science, Biotechnology Science, and Biological and Physical Science for Exploration, each guided by a Team Lead. According to the laboratory charter, our scientists (civil servants and on-site contractors) are expected to spend about one-half of their time on independent research aimed at the NASA goals and objectives, and the remaining half on project, program, or mission science supporting NASA flight and ground experiments and internal and external Principal Investigators. Because the selection agency for NASA competitive grants and the associated peer-review process is at NASA Headquarters rather than MSFC, our scientists (sometimes in collaboration with external investigators) compete for and win peer-reviewed flight and ground research grants. This selection process results in a high level of scientific expertise, enhances the reputation of our scientists, gives them practical experience and establishes credibility with the scientific community at large. The project science component of their work allows our organization to leverage a much larger research program at the national and international level to meet NASA's science objectives.

Simply put, the goal of the Microgravity Research Program is to do science (which is essentially finding out something previously unknown about nature) utilizing the unique long-term microgravity environment in Earth orbit. The objective of NASA's new "strategic research" program is to conduct scientific research that will provide safe and economical capabilities to enable humans to live, work and do science beyond Earth orbit. Our laboratory is focusing on strategic research areas that take the best advantage of the scientific assets that NASA has developed in our organization. For the Radiation Initiative we are developing and testing (in conjunction with other NASA Centers) computer codes that predict the radiation environment in space that humans will experience outside Earth's protective magnetic field and atmosphere. We are also using our materials science expertise to design and test new materials that have optimum radiation shielding and can also be utilized to build the spacecraft structure. In addition, we are working with other groups at MSFC to develop materials for Advanced Propulsion and integrating this research with Marshall's propulsion lead Center activities. Another "strategic research" area focuses on In-Space Fabrication and Repair. This research is directed toward enabling in-space materials processing for use in space. The goal of this program is to conduct scientific and technical research resulting in proof-of-concept experiments providing humans in space with an energy rich, resource rich, self-sustaining infrastructure at the earliest possible time and with minimum risk, launch mass and program cost. This research could support large space science experiments, human exploration, and space commercialization. Strategic biotechnology science research utilizes our laboratory's expertise in macromolecular biochemistry and protein structures to enable the determination of biologically critical structures (perhaps utilizing the benefits of microgravity experiments). The human body is constructed from and regulated with an elaborate set of macromolecular and protein building blocks. Knowing the structure of these blocks enables scientists to determine their function. Less than a third of these critical structures are known. Working in conjunction with other NASA

Centers whose work focuses on research at the cellular or organism level, we are applying our expertise to determine the structures critical to human survival beyond Earth orbit. In particular, we are working on the problems of human bone and muscle loss resulting from low gravity conditions, and radiation damage and repair in humans.

This Technical Memorandum documents the internal science research at our laboratory as presented in a review to Dr. Ann Whitaker, MSFC Science Director, in July 2002. These presentations have been revised and updated as appropriate for this report. It provides a "snapshot" of the internal science capability of our laboratory as an aid to other NASA organizations and the external scientific community.

2. RESEARCH

2.1 Biological and Physical Science for Exploration

The internal research activities of the "Exploration" team focus on basic materials science as well as strategic focal areas of research: multi-functional materials for radiation shielding, in-space fabrication and repair, and advance propulsion materials.

Basic materials science projects by team members focus on the experimental and theoretical study of basic physical properties of materials in various phases under microgravity conditions, e.g., the study of the viscosity of undercooled liquids, porosity of transparent materials, and solid-phase interfaces. Other projects focus on the characterization and application of the optical properties of composites.

On space radiation and shielding materials, the team, in collaborative projects with the MSFC Engineering Directorate (ED), is involved in the design, fabrication, and testing of polyethylene-based composites as multi-functional materials, for shielding as well as structural elements. Another collaborative project of the team, with the National Space Science and Technology Center (NSSTC), is developing a high-fidelity, high-energy charged particle detector for use on the Deep-Space Test Bed facility.

One in-space fabrication and repair effort of the team focuses on the feasibility of the use of mesoporous materials (aerogels) as casting molds.

Other projects in collaboration with the Transportation Directorate (TD) and ED focus on developing advanced materials for nuclear propulsion and include the study of the use of molybdenum-rhenium alloys for nuclear fuel containment and alumina-metal composites for propulsion system components.

2.1.1 Effect of Viscosity on the Crystallization of Undercooled Liquids

There have been numerous studies of glasses indicating that low-gravity processing enhances glass formation. NASA PI's are investigating the effect of low-g processing on the nucleation and crystal growth rates. Dr. Ethridge is investigating a potential mechanism for glass crystallization involving shear thinning of liquids in 1-g. For shear thinning liquids, low-g (low convection) processing will enhance glass formation. The study of the viscosity of glass forming substances at low shear rates is important to understand these new crystallization mechanisms.

The temperature dependence of the viscosity of undercooled liquids is also very important for NASA's containerless processing studies. In general, the viscosity of undercooled liquids is not known, yet knowledge of viscosity is required for crystallization calculations. Many researchers have used the Turnbull equation in error. Subsequent nucleation and crystallization calculations can be in error by many orders of magnitude. This demonstrates the requirement for better methods for interpolating and extrapolating the viscosity of undercooled liquids.

This is also true for undercooled water. Since amorphous water ice is the predominant form of water in the universe, astrophysicists have modeled the crystallization of amorphous water ice with viscosity relations that may be in error by five orders-of-magnitude.

For further information, see the presentation made by Dr. Edwin Ethridge in Appendix A, page E-1.

2.1.2 Basic and Applied Materials Science Research Efforts at MSFC Germane to NASA Goals

Presently, a number of investigations are ongoing that blend basic research with engineering applications in support of NASA goals. These include (1) "Pore Formation and Mobility (PFMI) – An *ISS* Glovebox Investigation" NASA Selected Project – 400-34-3D; (2) "Interactions Between Rotating Bodies" Center Director's Discretionary Fund (CDDF) Project – 279-62-00-16; (3) "Molybdenum – Rhenium (Mo-Re) Alloys for Nuclear Fuel Containment" TD Collaboration – 800-11-02; (4) "Fabrication of Alumina – Metal Composites for Propulsion Components" ED Collaboration – 090-50-10; (5) "Radiation Shielding for Deep-Space Missions" SD Effort; (6) "Other Research".

In brief, "Pore Formation and Mobility" is an experiment to be conducted in the *ISS* Microgravity Science Glovebox that will systematically investigate the development, movement, and interactions of bubbles (porosity) during the controlled directional solidification of a transparent material. In addition to promoting our general knowledge of porosity physics, this work will serve as a guide to future *ISS* experiments utilizing metal alloys. "Interactions Between Rotating Bodies" is a CDDF sponsored project that is critically examining, through theory and experiment, claims of "new" physics relating to gravity modification and electric field effects. "Molybdenum – Rhenium Alloys for Nuclear Fuel Containment" is a TD collaboration in support of nuclear propulsion. Mo-Re alloys are being evaluated and developed for nuclear fuel containment. "Fabrication of Alumina – Metal Composites for Propulsion Components" is an ED collaboration with the intent of increasing strength and decreasing weight of metal engine components through the incorporation of nanometer-sized alumina fibers. "Radiation Shielding for Deep-Space Missions" is an SD effort aimed at minimizing the health risk from radiation to human space voyagers; work to date has been primarily programmatic but experiments to develop hydrogen-rich materials for shielding are planned. "Other Research" includes BUNDLE (Bridgman Unidirectional Dendrite in a Liquid Experiment) activities (primarily crucible development), vibrational float-zone processing (with Vanderbilt University), use of ultrasonics in materials processing (with UAH), rotational effects on microstructural development, and application of magnetic fields for mixing.

For further information, see the presentation made by Dr. Richard Grugel in Appendix A, page E-14.

2.1.3 Development of Aerogel Molds for Metal Casting Using Lunar and Martian Regolith

In the last few years NASA has set new priorities for research and development of technologies necessary to enable long-term presence on the Moon and Mars. Among these key technologies is what is known as *in situ* resource utilization, which defines all conceivable usage of mineral, liquid, gaseous, or biological resources on a visited planet. In response to this challenge, we have been focusing on developing and demonstrating the manufacturing of a specific product using Lunar and Martian soil simulants (i.e., a mold for the casting of metal and alloy parts) which will be an indispensable tool for the survival of outposts on the Moon and Mars. In addition, our purpose is to demonstrate the feasibility of using mesoporous materials such as aerogels to serve as efficient casting molds for high quality components in propulsion and other aerospace applications.

The first part of the project consists of producing aerogels from the *in situ* resources available in Martian and Lunar soil. The approach we are investigating is to use chemical processes to solubilize silicates using organic reagents at low temperatures and then use these as precursors in the formation of aerogels for the fabrication of metal casting molds. One set of experiments consists of dissolving silica sources in basic ethylene glycol solution to form silicon glycolates. When ground silica aerogel was used as source material, a clear solution of silicon glycolate was obtained and reacted to form a gel thus proving the feasibility of this approach. The application of this process to Lunar and Martian simulants did not result in the formation of a gel; further study is in progress. In the second method acidified alcohol is reacted with the simulants to form silicate esters. Preliminary results indicate the presence of silicon alkoxide in the product distillation. However, no gel has been obtained so further characterization is ongoing.

In the second part of the project, the focus has been on developing a series of aerogel plates suitable for thin plate metal casting and ingot metal castings. The influence of aerogels on thin wall metal castings was studied by placing aerogel plates into the cavities of thin sections of resin bonded sand molds. An A1 based commercial alloy (A356) containing 7 percent Si was poured into these molds. Post-solidification studies provide evidence that aerogel inserts significantly reduce the cooling rate during solidification. The advantage of a lower rate using aerogel inserts was reflected in the reduction of casting defects such as shrinkage porosity. Quantitative results support the hypothesis that using aerogels as a mold material can offer definite advantages when used as casting thin sections.

As a separate effort, silica aerogel with cylindrical cavities have been prepared and will be evaluated for casting commercial alloys.

For further information, see the presentation made by Dr. Benjamin Penn in Appendix A, page E-23.

2.1.4 Graphite/ Ultra-High Modulus Polyethylene Hybrid Fiber Composites with Epoxy and Polyethylene Matrices for Cosmic Radiation Shielding

(Proposal submitted in response to NRA-01-OBPR-05)

One of the most significant technical challenges in long-duration space missions is that of protecting the crew from harmful radiation. Protection against such radiation on a manned Mars mission will be of vital importance both during transit and while on the surface of the planet. The development of multifunctional materials that serve as integral structural members of the space vehicle and provide the necessary radiation shielding for the crew would be both mission enabling and cost effective. Additionally, combining shielding and structure could reduce total vehicle mass. Hybrid laminated composite materials having both ultramodulus polyethylene (PE) and graphite fibers in epoxy and PE matrices could meet such mission requirements. PE fibers have excellent physical properties, including the highest specific strength of any known fiber. Moreover, the high hydrogen (H) content of polyethylene makes the material an excellent shielding material for cosmic radiation. When such materials are incorporated into an epoxy or PE matrix a very effective shielding material is expected. Boron (B) may be added to the matrix resin or used as a coating to further increase the shielding effectiveness due to B's ability to slow thermal neutrons. These materials may also serve as micrometeorites shields due to PE's high impact energy absorption properties. It should be noted that such materials can be fabricated by existing equipment and methods. It is the objective of this work therefore to: (a) perform preliminary analysis of the radiation transport within these materials; (b) fabricate panels for mechanical property testing before and after radiation exposure. Preliminary determination on the effectiveness of the combinations of material components on both shielding and structural efficiency will be made.

For further information, see the presentation made by Dr. Benjamin Penn in Appendix A, page E-29.

2.1.5 Program for the Increased Participation of Minorities in NASA-Related Research

(NASA Administrator's Fellowship Program for 2002)

The goal of this program is to increase the participation of minorities in NASA related research and "Science for the Nation's Interest". Collaborative research projects will be developed involving NASA-MSFC, National Space Science and Technology Center (NSSTC), other government agencies, industries and minority serving institutions (MSIs). The primary focus for the MSIs will be on Alabama A&M University and Tuskegee University, which are in partnership with the NSSTC. These schools have excellent Ph.D. programs in physics and materials science and engineering, respectively. The first phase of this program will be carried out at Alabama A&M University in the "Research and Development Office" in collaboration with Dr. Dorothy Huston, Vice President of Research and Development. The development assignment will be carried out at the NSSTC with Sandy Coleman/ RS01 and this will primarily involve working with Tuskegee University.

A portion of the program will be devoted to identifying and contacting potential funding sources for use in establishing collaborative research projects between NASA-MSFC, other government agencies, NSSTC, industries, and MSIs. These potential funding sources include the National Science Foundation (NSF), National Institute of Health (NIH), Department of Defense (DOD), Army, Navy, and Air Force. Collaborative research projects will be written mostly in the following research areas:

a. Cosmic radiation shielding materials
b. Advanced propulsion material
c. Biomedical materials and biosensors
d. *In situ* resource utilization
e. Photonics for NASA applications

For further information, see the presentation made by Dr. Benjamin Penn in Appendix A, page E-35.

2.1.6 Advanced Technology Development: Solid-Liquid Interface Characterization Hardware

Characterizing the solid-liquid interface during directional solidification is key to understanding and improving material properties. The goal of this Advanced Technology Development (ATD) has been to develop hardware, which will enable real-time characterization of practical materials, such as aluminum (Al) alloys, to unprecedented levels. Required measurements include furnace and sample temperature gradients, undercooling at the growing interface, interface shape, or morphology, and furnace translation and sample growth rates (related). These and other parameters are correlated with each other and time. A major challenge was to design and develop all of the necessary hardware to measure the characteristics, nearly simultaneously, in a smaller integral furnace compatible with existing X-ray Transmission Microscopes, XTMs.

Most of the desired goals have been accomplished through three generations of Seebeck furnace brassboards, several varieties of film thermocouple arrays, heaters, thermal modeling of the furnaces, and data acquisition and control (DAC) software. Presentations and publications have resulted from these activities, and proposals to use this hardware for further materials studies have been submitted as sequels to this last year of the ATD.

For further information, see the presentation made by Dr. Palmer Peters in Appendix A, page E-39.

2.1.7 Nanophase and Composite Optical Materials

This talk will focus on accomplishments, current developments, and future directions of our work on composite optical materials for microgravity science and space exploration. This research spans the order parameter from quasi-fractal structures such as sol-gels and other aggregated or porous media, to statistically random cluster media such as metal colloids, to highly ordered materials such as layered media and photonic bandgap materials. The common focus is on flexible materials that can be used to produce composite or artificial materials with superior optical properties that could not be achieved with homogeneous materials. Applications of this work to NASA exploration goals such as terraforming, biosensors, solar sails, solar cells, and vehicle health monitoring, will be discussed.

For further information, see the presentation made by Dr. David Smith in Appendix A, page E-57.

2.1.8 Silicon Detector System for Cross Section Measurements

In order to estimate the radiation shielding effectiveness of materials it is necessary to know cosmic ray particles are broken up as they pass though these materials. The breakup of cosmic ray particles is characterized by the nuclear fragmentation cross sections, i.e. an effective geometrical cross section assigned to each target nucleus that represents its apparent size for fragmenting the incident particle. The values of these cross sections depend on the details of nuclear physics and cannot be calculated from first principles owing to the many-body nature of the interactions. The only way to determine them is to measure them. Once a sufficient number of cross sections have been measured, the systematic nature of the interactions allows other cross-sections to be estimated. The number of cross sections that contribute to the estimation of shielding effectiveness is very large ≈10,000. Fortunately most make minor contributions. These can be estimated from nuclear systematics. Only those who's uncertainties make significant contributions to the error in the shielding effectiveness estimations need to be measured.

In the past it has proven difficult to measure light fragment production cross sections from the interactions of heavy cosmic rays owing to the size of the detectors used. We have developed a highly pixilated silicon (Si) detector system that can individually identify these light fragments while making efficient use of costly accelerator time. This system is an outgrowth of detector technology developed under a CDDF and a Code S sponsored cosmic ray experiment.

For further information, see the presentation made by Dr. James Adams in Appendix A, page E-68.

2.2 Materials Science

The Materials Science Program is structured so that NASA's headquarters is responsible for the program content and selection, through the Enterprise Scientist, and MSFC provides for implementation of ground and flight programs with a Discipline Scientist and Discipline Manager. The Discipline Working Group of eminent scientists from outside of NASA acts in an advisory capacity and writes the Discipline Document from which the NRA content is derived. The program is reviewed approximately every three years by groups such as the Committee on Microgravity Research, the National Materials Advisory Board, and the OBPR Maximization and Prioritization (ReMaP) Task Force.

The flight program has had as many as twenty-six principal investigators (PIs) in flight or flight definition stage, with the numbers of PIs in the future dependent on the results of the ReMaP Task Force and internal reviews. Each project has a NASA-appointed Project Scientist, considered a half-time job, who assists the PI in understanding and preparing for internal reviews such as the Science Concept Review and Requirements Definition Review. The Project Scientist also insures that the PI gets the maximum science support from MSFC, represents the PI to the MSFC community, and collaborates with the Project Manager to insure the project is well-supported and remains vital. Currently available flight equipment includes the Materials Science Research Rack (MSRR-1) and Microgravity Science Glovebox.

Ground based projects fall into one or more of several categories. Intellectual Underpinning of Flight Program projects include theoretical studies backed by modeling and computer simulations; bring to maturity new research, often by young researchers, and may include preliminary short duration low gravity experiments in the KC-135 aircraft or drop tube; enable characterization of data sets from previous flights; and provide thermophysical property determinations to aid PIs. Radiation Shielding and preliminary *In Situ* Resource Utilization (ISRU) studies work towards future long duration missions. Biomaterials support materials issues affecting crew health. Nanostructured Materials are currently considered to be maturing new research, and Advanced Materials for Space Transportation has as yet no PIs. PIs are assigned a NASA Technical Monitor to maintain contact, a position considered to be a 5 percent per PI effort.

Currently 33 PIs are supported on the 1996 NRA, which is about to expire, and 59 on the 1998 NRA. Two new NRAs, one for Radiation Shielding and one for Materials Science for Advanced Space Propulsion are due to be announced by the 2003 fiscal year.

MSFC has a number of facilities supporting materials science. These include the Microgravity Development Laboratory/SD43; Electrostatic Levitator Facility; SCN Purification Facility; Electron Microscope/Microprobe Facility; Static and Rotating Magnetic Field Facility; X-Ray Diffraction Facility; and the Furnace Development Laboratory.

2.2.1 Reduction of Defects in Germanium-Silicon

(Flight experiment awarded by 96 NRA, SCR completed in December 2000)

Crystals grown without contact with a container have far superior quality to otherwise similar crystals grown in direct contact with a container. In addition to float-zone processing, detached-Bridgman growth is a promising tool to improve crystal quality, without the limitations of float zoning or the defects introduced by normal Bridgman growth. Goals of this project include the development of the detached Bridgman process to be reproducible and well understood and to quantitatively compare the defect and impurity levels in crystals grown by these three methods. Germanium (Ge) and germanium-silicon (Ge-Si) alloys are being used. At MSFC, we are responsible for the detached Bridgman experiments intended to differentiate among proposed mechanisms of detachment, and to confirm or refine our understanding of detachment. Because the contact angle is critical to determining the conditions for detachment, the sessile drop method was used to measure the contact angles as a function of temperature and composition for a large number of substrates made of potential ampoule materials. Growth experiments have used pyrolytic boron nitride (pBN) and fused silica ampoules with the majority of the detached results occurring predictably in the pBN. Etch pit density (EPD) measurements of normal and detached Bridgman-grown Ge samples show a two order of magnitude improvement in the detached-grown samples. The nature and extent of detachment is determined by using profilometry in conjunction with optical and electron microscopy. The stability of detachment has been analyzed, and an empirical model for the conditions necessary to achieve sufficient stability to maintain detached growth for extended periods has been developed. We have investigated the effects on detachment of ampoule material, pressure difference above and below the melt, and Si concentration; samples that are nearly completely detached can be grown repeatedly in pBN. Current work is concentrated on developing a method to make in situ pressure measurements in the growth ampoules.

For further information, see the presentation made by Dr. Frank Szofran in Appendix B, page M-9.

2.2.2 Effects of Traveling Magnetic Field on Dynamics of Solidification

The Lorentz body force induced in electrically conducting fluids can be utilized for a number of materials processing technologies. An application of strong static magnetic fields can be beneficial for damping convection present during solidification. On the other hand, alternating magnetic fields can be used to reduce as well as to enhance convection. However, only special types of time dependent magnetic fields can induce a non-zero time averaged Lorentz force needed for convection control. One example is the rotating magnetic field. This field configuration induces a swirling flow in circular containers. Another example of a magnetic field configuration is the traveling magnetic field (TMF). It utilizes axisymmetric magnetostatic waves. This type of field induces an axial recirculating flow that can be advantageous for controlling axial mass transport, such as during solidification in long cylindrical tubes. Incidentally, this is the common geometry for crystal growth research. The Lorentz force induced by TMF can potentially counter-balance the buoyancy force, diminishing natural convection, or even setting up the flow in reverse direction. Crystal growth process in presence of TMF can be then significantly modified. Such properties as the growth rate, interface shape and macro segregation can be affected and optimized. Melt homogenization is the other potential application of TMF. It is a necessary step prior to solidification. TMF can be attractive for this purpose, as it induces a basic flow along the axis of the ampoule. TMF can be a practical alloy mixing method especially suited for solidification research in space. In the theoretical part of this work, calculations of the induced Lorentz force in the whole frequency range have been completed. The basic flow characteristics for the finite cylinder geometry are completed and first results on stability analysis for higher Reynolds numbers are obtained. A theoretical model for TMF mixing is also developed. In the experimental part, measurements of flow induced by TMF in a column of mercury (Hg) are presented. Also, an alloy mixing of Bi-Sn of the eutectic composition is demonstrated. A traveling magnetic field of 4mT at 3kHz applied for 120 minutes is found to be sufficient to homogenize an alloy enclosed in a 1cm diameter and 12 cm long tube.

For further information, see the presentation made by Dr. Konstantin Mazuruk in Appendix B, page M-27.

2.2.3 Uses of Computed Tomography for Characterizing Materials Grown Terrestrially and in Microgravity

Computed Tomography (CT) has proved to be of inestimable use in providing a rapid evaluation of a variety of samples from Mechanics of Granular Materials (MGM) to electronic materials (Ge-Si alloys) to space grown materials such as meteorites. The system at Kennedy Space Center (KSC), because of its convenient geographical location, is ideal for examining samples before launch and immediately after returning to Earth. It also has the advantage of the choice of fluxes, and in particular the use of a radioactive cobalt source, which is basically monochromatic. This permits a reasonable measurement of density to be made from which chemical composition can be determined. Due to the current dearth of long duration space grown materials, the CT instrument has been used (1) to characterize materials in preparation for flight, (2) to determine thermal expansion values, and (3) to examine long duration space grown materials, i.e. meteorites.

This work will first describe the establishment of the protocol for obtaining the optimum density readings for any material. Included will be the effects of the hardware or instrumental parameters that can be controlled, and the techniques used to process the CT data. Examples will be given of the compositional variation along a single crystal of Ge-Si alloy.

Density variation with temperature has been measured in preparation for future materials science experiments; this involved the fabrication at MSFC and installation of a single zone furnace at KSC incorporating a heat pipe to ensure high temperature uniformity. At the time of writing the thermal expansion of lead (Pb) has been measured from room temperature to 900°C. Three methods are available. Digital radiography enables length changes to be determined. Prior to melting the sample is smaller than the container and the diameter change can be measured. Most critical, however, is the density change in solid, through the melting region, and in the liquid state. These data are needed for engineering purposes to aid in the design of containment cartridges, and for enabling fluid flow calculations. A second sample, with the Pb alloyed with Sb is ready for scanning. This corresponds to the planned composition of Dr. Poirier's flight experiment. Other materials pertinent to NASA programs such as Al-Cu (Trivedi), CdTe (Banish), HgCdTe (Lehoczky) will be examined below and above the melting point.

Finally, three-dimensional results will be shown of the structure of a two-phase metallic meteorite of metal and sulfide, in which the Fe-Ni phase has coarsened during slow cooling over hundreds of millions of years.

For further information, see the presentation made by Dr. Donald Gillies in Appendix B, page M-44.

2.2.4 An Overview of Materials Science Research at the Marshall Space Flight Center Electrostatic Levitator Facility and Recent CDDF Efforts

Containerless processing is an important tool for materials research. The freedom from a crucible allows processing of liquid materials in a metastable undercooled state, as well as allowing processing of high temperature and highly reactive melts. Electrostatic levitation (ESL) is a containerless method which provides a number of unique advantages, including the ability to process non-conducting materials, the ability to operate in ultra-high vacuum or at moderate gas pressure (≈5 atm), and the decoupling of positioning force from sample heating. ESL also has the potential to reduce internal flow velocities below those possible with electromagnetic, acoustic, or aero-acoustic techniques. In electrostatic levitation, the acceleration of gravity (or residual acceleration in reduced gravity) is opposed by the action of an applied electric field on a charged sample. Microgravity allows electrostatic levitation to work even more effectively. The ESL facility at NASA's Marshall Space Flight Center is in use for materials research and thermophysical property measurement by a number of different internal and external investigators. Results from the recent CDDF studies on the high energy X-ray beamline at the Advanced Photon Source of Argonne National Laboratory will be presented. The Microgravity Research Program supports the facility.

For further information, see the presentation made by Dr. Jan Rogers in Appendix B, page M-62.

2.2.5 The Role of Convection and Growth Competition on Phase Selection in Microgravity

For a wide range of compositions, Fe-Cr-Ni alloys can solidify by a two-step process: a metastable solid forms first, subsequently transforming into the stable solid phase. This two-step solidification produces a profoundly different microstructure, and therefore different properties, in the final solid.

The delay time between the two steps of the solidification process varies from microseconds to seconds. This delay time is a strong function of composition and a weak function of the undercooling of the melt below the metastable liquidus. From the results obtained during the MSL-1 mission and in ground based electrostatic levitation testing at NASA MSFC, we know that convection also has a significant effect on the delay time. By examining the effect of convection on delay time over a wide range of convection, for several different alloys, we can gain a better understanding and better control of the microstructural evolution and final structure of stainless steel alloys.

MSFC provides ESL for ground-based testing in a low-convection state, and the numerical modeling that enables estimation of the convection levels under the different process conditions.

For further information, see the presentation made by Dr. Robert Hyers for Dr. Merton Flemings in Appendix B, page M-81.

2.2.6 Studies of Nucleation and Growth, Specific Heat and Viscosity of Undercooled Melts of Quasicrystals and Polytetrehedral-Phase-Forming Alloys

By investigating the properties of quasicrystals and quasicrystal-forming liquid alloys, we may determine the role of ordering of the liquid phase in the formation of quasicrystals, leading to a better fundamental understanding of both the quasicrystal and the liquid. A quasicrystal is solid characterized by a symmetric but non-periodic arrangement of atoms, usually in the form of an icosahedron (12 atoms, 20 triangular faces). It is theorized that the short-range order in liquids takes this same form. The degree of ordering depends on the temperature of the liquid, and affects many of the liquid's properties, including specific heat, viscosity, and electrical resistivity.

The MSFC role in this project includes solidification studies, phase diagram determination, and thermophysical property measurements on the liquid quasicrystal-forming alloys, all by electrostatic levitation (ESL). The viscosity of liquid quasicrystal-forming alloys is measured by the oscillating drop method, both in the stable and undercooled liquid state. The specific heat of solid, undercooled liquid, and stable liquid are measured by the radiative cooling rate of the droplets.

For further information, see the presentation made by Dr. Robert Hyers for Professor Kenneth Kelton in Appendix B, page M-94.

2.2.7 Succinonitrile Purification Facility

The Succinonitrile (SCN) Purification Facility provides succinonitrile and succinonitrile alloys to several NRA selected investigations for flight and ground research at various levels of purity. The purification process employed includes both distillation and zone refining. Once the appropriate purification process is completed, samples are characterized to determine the liquidus and/or solidus temperature, which is then related to sample purity. The lab has various methods for measuring these temperatures with accuracies in the milliKelvin to tenths of milliKelvin range. The ultra-pure SCN produced in our facility is indistinguishable from the standard material provided by NIST to well within the stated +/- 1.5mK of the NIST triple point cells.

In addition to delivering material to various investigations, our current activities include process improvement, characterization of impurities and triple point cell design and development. The purification process is being evaluated for each of the four vendors to determine the efficacy of each purification step. We are also collecting samples of the remainder from distillation and zone refining for analysis of the constituent impurities. The large triple point cells developed will contain SCN with a melting point of 58.0642°C +/- 1.5mK for use as a calibration standard for Standard Platinum Resistance Thermometers (SPRTs).

For further information, see the presentation made by Louise Strutzenberg in Appendix B, page M-104.

2.2.8 Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

(Flight experiment awarded by 94NRA)

The objective of the project is to determine the relative contributions of gravity-driven fluid flows to the compositional distribution, incorporation of impurities and defects, and deviation from stoichiometry observed in the crystals grown by vapor transport as results of buoyancy-driven convection and growth interface fluctuations caused by irregular fluid-flows. ZnSe and related ternary compounds, such as ZnSeS and ZnSeTe, were grown by vapor transport technique with real time *in situ* non-invasive monitoring techniques. The grown crystals were characterized extensively to correlate the grown crystal properties with the growth conditions. Significant effects of gravity vector orientation on the growth crystal morphology and point defect distribution were observed.

For further information, see the presentation made by Dr. Ching-Hua Su in Appendix B, page M-108.

2.2.9 Structural Fluctuation and Thermophysical Properties of Molten II-VI Compounds

(A ground-based project awarded by 98NRA)

The objectives of the project is to conduct ground-based experimental and theoretical research on the structural fluctuations and thermophysical properties of molten II-VI compounds to enhance the basic understanding of the existing flight experiments in microgravity materials science programs and to study the fundamental heterophase fluctuations phenomena in these melts by:

1. conducting neutron scattering analysis and measuring quantitatively the relevant thermophysical properties of the II-VI melts such as viscosity, electrical conductivity, thermal diffusivity and density as well as the relaxation characteristics of these properties to advance the understanding of the structural properties and the relaxation phenomena in these melts and
2. performing theoretical analyses on the melt systems to interpret the experimental results.

All the facilities required for the experimental measurements have been procured, installed and tested. A relaxation phenomenon, which shows a slow drift of the measured thermal conductivity toward the equilibrium value after cooling of the sample, was observed for the first time. An apparatus based on the transient torque induced by a rotating magnetic field has been developed to determine the viscosity and electrical conductivity of semiconducting liquids. Viscosity measurements on molten tellurium showed similar relaxation behavior as the measured diffusivity. Neutron scattering experiments were performed on the HgTe and HgZnTe melts and the results on pair distribution showed better resolution than previous reported.

For further information, see the presentation made by Dr. Ching-Hua Su in Appendix B, page M-126.

2.2.10 Laboratory and In-Flight, *In situ* X-ray Imaging and Scattering Facility for Materials, Biotechnology and Life Sciences

(Instrument Technology Development (ITD) project)

We propose a multifunctional X-ray facility for the Materials, Biotechnology and Life Sciences Programs to visualize formation and behavior dynamics of materials, biomaterials, and living organisms, tissues and cells. The facility will combine X-ray topography, phase micro-imaging and scattering capabilities with sample units installed on the goniometer. This should allow, for the first time, to monitor under well defined conditions, *in situ*, in real time: creation of imperfections during growth of semiconductors, metal, dielectric and biomacromolecular crystals and films, high-precision diffraction from crystals within a wide range of temperatures and vapor, melt, solution conditions, internal morphology and changes in living organisms, tissues and cells, diffraction on biominerals, nanotubes and particles, radiation damage, also under controlled formation/life conditions.

The system will include an ultrabright X-ray source, X-ray mirror, monochromator, image-recording unit, detectors, and multipurpose diffractometer that fully accommodate and integrate furnaces and samples with other experimental environments. The easily adjustable laboratory and flight versions will allow monitoring processes under terrestrial and microgravity conditions. The flight version can be made available using a microsource combined with multilayer or capillary optics.

For further information, see the presentation made by Dr. Ching-Hua Su in Appendix B, page M-142.

2.2.11 Evolution of Local Microstructures: Spatial Instabilities in Coarsening Clusters

Diffusion-limited capillarity-driven coarsening of precipitates is an important and intensively studied phenomenon. The classic coarsening theory developed by Lifshitz and Syozov and Wagner (LSW theory) is limited to infinitesimally small volume fractions, V_v, therefore neglects all direct inter-particle interactions. This work uses modeling and holographic imaging to compare coarsening rates in "high" volume fraction versus low volume fraction microstructures by observing mixed-dimensional droplets (spherical caps on a surface coarsening by two-dimensional diffusion) during ground-based investigations. The method involves filling a cell with selected homogeneous parent phase, and cooling below the consolute temperature to the isopycnic temperature in the two-phase region of a monotectic system. A microgravity holographic experiment is required for three-dimensional observations to minimize sedimentation during long-term coarsening.

Determination of sizes and positions of the many droplets in the holographic images requires automation. We have developed software for automated data analysis, and demonstrated good agreement between regenerated maps and scaled photographs of the original holograms for mixed-dimensional coarsening.

The results of these experiments were presented in a formal microgravity Science Concept Review (SCR) on December 18, 2000.

For further information, see the presentation made by Dr. Donald Frazier in Appendix B, page M-146.

2.2.12 Spaceflight Holography Investigation in a Virtual Apparatus

The movement of a particle in a fluid is one of the most fundamental processes in physics and plays an important role in materials science. For example, the physics of crystal growth from a nucleation site in solution can be dominated by movement of the solution over the crystal surface. Gravity usually dominates the equations of motion, but in microgravity other terms can dominate, making the equation much more complex. Until recently, the equations were solved only by numerical methods and/or by neglecting terms. During this study, we discovered an exact solution to the equations, which shows that the usually neglected terms become extremely important in microgravity. We also developed diagnostic recording methods using holography to save all of the particle field data, allowing the experiment to essentially be transferred from space back to earth in what we call the "virtual apparatus". We will record holograms of particle distributions in motion in microgravity and bring them back to earth for analysis, allowing the study of the full three-dimensional motion of sets of particles, allowing us to test the new analytical solutions. The experiment will also provide accurate measurements of the quasi-steady acceleration of the space platform and other interesting microgravity and g-jitter effects. This program will produce the flight definition for an experiment in the microgravity environment of space to validate the theoretical model. We will design an experiment with the help of the theoretical model that is optimized for testing the model, measuring g, g-jitter, and other microgravity phenomena.

For further information, see the presentation made by William Witherow in Appendix B, page M-159.

2.2.13 Particle Engulfment and Pushing by Solidifying Interfaces

The study of particle behavior at solid/liquid interfaces (SLI's) is at the center of the Particle Engulfment and Pushing (PEP) research program. Interactions of particles with SLI's have been of interest since the 1960's, starting with geological observations, i.e., frost heaving. Ever since, this field of research has become significant to such diverse areas as metal matrix composite materials, fabrication of superconductors, and inclusion control in steels. The PEP research effort is geared towards understanding the fundamental physics of the interaction between particles and a planar SLI. Experimental work including 1-g and μ-g experiments accompany the development of analytical and numerical models.

The experimental work comprised of substantial groundwork with aluminum (Al) and zinc (Zn) matrices containing spherical zirconia particles, μ-g experiments with metallic Al matrices and the use of transparent organic metal-analogue materials. The modeling efforts have grown from the initial steady-state analytical model to dynamic models, accounting for the initial acceleration of a particle at rest by an advancing SLI. To gain a more comprehensive understanding, numerical models were developed to account for the influence of the thermal and solutal field. Current efforts are geared towards coupling the diffusive 2-D front tracking model with a fluid flow model to account for differences in the physics of interaction between 1-g and μ-g environments. A significant amount of this theoretical investigation has been and is being performed by co-investigators at NASA MSFC.

The impetus of the first μ-g experiment (LMS, 1996) with metallic matrices was the proof of concept and technical feasibility. The second μ-g experiments (USMP-4, 1997) with organic materials yielded a substantial database for the evaluation of PEP theoretical models. For the LMS mission pre- and post-processing characterization of metallic samples, including distribution of zirconia particles, were carried out at MSFC using the unique X-ray Transmission Microscope. For the USMP-4 glovebox experiment, design of hardware and proof of concept experiments on parabolic flights was carried out by co-investigators at MSFC.

Current efforts are geared towards the development of suitable ampoules for planned experiments on board the *International Space Station* (*ISS*), in conjunction with verification of the thermal requirements of the Quench Module Insert (QMI) furnace module. MSFC is supporting the PI in developing a validated furnace thermal model to assist him in his ampoule design and currently tests are being performed to evaluate the performance of the *ISS* furnace insert.

For further information, see the presentation made by Dr. Subhayu Sen in Appendix B, page M-173.

2.2.14 Numerical Modeling and Fluids Experiments for Materials Processing and Protein Crystallization

The presentation highlights two of the three NASA funded projects currently in progress under this task:

1. Principal Investigator: Study of Fluid Flow Control in Protein Crystallization Using Strong Magnetic Fields. CoIs: F. Leslie and E. Ciszak - Fluid physics NRA

2. Co Investigator: Fundamental Studies of Crystal Growth of Microporous Materials, Flight definition research grant with Dr. Prabir Dutta, PI, The Ohio State University

Included here is a brief outline of the protein crystallization project (Co Investigator: Crystal Growth of ZnSe and related Ternary Compound Semiconductors by Vapor Transport with Dr. Ching-Hua Su, PI, NASA MSFC).

Introduction: An important component in biotechnology, particularly in the area of protein engineering and rational drug design is the knowledge of the precise three-dimensional molecular structure of proteins. The quality of structural information obtained from X-ray diffraction methods is directly dependent on the degree of perfection of the protein crystals. As a consequence, the growth of high quality macromolecular crystals for diffraction analyses has been the central focus for biochemists, biologists, and bioengineers.

Macromolecular crystals are obtained from solutions that contain the crystallizing species in equilibrium with higher aggregates, ions, precipitants, other possible phases of the protein, foreign particles, the walls of the container, and a likely host of other impurities. By changing transport modes in general, i.e., reduction of convection and sedimentation, as is achieved in “microgravity”, we have been able to dramatically affect the movement and distribution of macromolecules in the fluid, and thus their transport, formation of crystal nuclei, and adsorption to the crystal surface. While a limited number of high quality crystals from space flights have been obtained, as the recent National Research Council (NRC) review of the NASA microgravity crystallization program pointed out, the scientific approach and research in crystallization of proteins has been mainly empirical yielding inconclusive results [1].

Hypothesis: We postulate that we can reduce convection in ground-based experiments and we can understand the different aspects of convection control through the use of strong magnetic fields and field gradients. We postulate that limited convection in a magnetic field will provide the environment for the growth of high quality crystals. The approach exploits the variation of fluid magnetic susceptibility with concentration for this purpose and the convective damping is realized by appropriately positioning the crystal growth cell so that the magnetic susceptibility force counteracts terrestrial gravity.

Objective: The general objective is to test the hypothesis of convective control using a strong magnetic field and magnetic field gradient and to understand the nature of the various forces that come into play. Specifically we aim to delineate causative factors and to quantify them through experiments, analysis and numerical modeling. Once the basic understanding is obtained, the study will focus on testing the hypothesis on proteins of pyruvate dehydrogenase complex (PDC), proteins E1 and E3.

Obtaining high crystal quality of these proteins is of great importance to structural biologists since their structures need to be determined. Our approach will simultaneously provide the first implementation of our flow control hypotheses and investigation.

Specific goals for the investigation are:

1. To develop an understanding of convection control in diamagnetic fluids with concentration gradients through experimentation and numerical modeling. Specifically solutal buoyancy driven convection due to crystal growth will be considered.
2. To develop predictive measures for successful crystallization in a magnetic field using analyses and numerical modeling for use in future protein crystal growth experiments. This will establish criteria that can be used to estimate the efficacy of magnetic field flow damping on crystallization of candidate proteins.
3. To demonstrate the understanding of convection damping by high magnetic fields to a class of proteins that is of interest and whose structure is as yet not determined.
4. To compare quantitatively, the quality of the grown crystals with and without a magnetic field. X-ray diffraction techniques will be used for the comparative studies.

Value: The proposed work is ground-based with both theoretical and experimental investigation of crystallization phenomena with emphasis on the important fluid physics element of the protein crystallization process. Further, the proposed investigation employs an interdisciplinary approach to advance the research in the important area of biocrystallization and thus biotechnology. Understanding the fluid flow due to solutal buoyancy convection and controlling that flow through the application of a strong magnetic field and field gradient are important objectives. This implies obtaining quantitative information through carefully conducted experiments, developing predictive capability through analytical and numerical simulations, and applying it to proteins whose structures are as yet undetermined. The studies will directly provide a predictive tool and a technique to further reduce convective contamination in space experiments on board the *ISS*.

Our research will determine whether the use of a strong magnetic field has significant impact on the crystallization of the most challenging macromolecular systems. Extending our success in crystallization in a magnetic field with proteins from arguably the most exciting and challenging multienzyme assembly of the human body, i.e. pyruvate dehydrogenase complex will certainly provide a breakthrough for macromolecular crystal growers.

[1.] National Research Council, Space Studies Board, Commission on Physical Sciences, Mathematics and Applications, in Future Biotechnology Research on the International Space Station, national Academy Press, Washington, DC., 2000, 10-16.

For further information, see the presentation made by Dr. Narayanan Ramachandran in Appendix B, page M-184.

2.3 Biotechnology Science

MSFC has several areas of in-house research in biotechnology. These include crystal growth defects, crystallization hardware development, structural biology, cell biology, and new methods for studying crystallization and fluid dynamics. Funded or science program supported research projects in these areas look at microgravity-unique reasons for space crystals, developing modeling for user-assistance, advancing in-house structures for flight and science, muscle physiology and cancer risk assessment for the Department of Defense, light scattering, atomic force microscopy, and new uses for old techniques.

2.3.1 Flight Hardware Development and Research at MSFC for Optimizing Success on the *International Space Station*

To optimize biological crystallization success in microgravity in-house personnel at the MSFC are working on the development of innovative flight hardware such as Delta-L and the Iterative Biological Crystallization (IBC) apparatus as well as troubleshooting the performance of existing hardware.

Delta-L will provide a diagnostic hardware to examine the relationship between crystal growth characteristics and crystal quality improvement in microgravity. IBC is a new hardware being designed to allow iteration of crystal growth experiments in microgravity using innovative 'lab on a chip' technology. While being built to obtain scientific data of benefit to the scientific community, the design methods involved in the development of these hardware have directly benefited other groups within NASA and keep NASA at the forefront of innovation.

For further information, see the presentation made by Dr. Russell Judge in Appendix C, page B-2.

2.3.2 Structural Biology of Proteins of the Multienzyme Assembly Human Pyruvate Dehydrogenase Complex

Objectives and research challenges of this effort include:

1. Need to establish Human Pyruvate Dehydrogenase Complex protein crystals
2. Need to test value of microgravity for improving crystal quality of Human Pyruvate Dehydrogenase Complex protein crystals
3. Need to improve flight hardware in order to control and understand the effects of microgravity on crystallization of Human Pyruvate Dehydrogenase Complex proteins
4. Need to integrate sets of national collaborations with the restricted and specific requirements of flight experiments
5. Need to establish a highly controlled experiment in microgravity with a rigor not yet obtained
6. Need to communicate both the rigor of microgravity experiments and the scientific value of results obtained from microgravity experiments to the national community
7. Need to advance the understanding of Human Pyruvate Dehydrogenase Complex structures so that scientific and commercial advance is identified for these proteins

For further information, see the presentation made by Dr. Ewa Ciszak in Appendix C, page B-10.

2.3.3 Cell Science and Cell Biology Research at MSFC: Summary

The common theme of these research programs is that they investigate regulation of gene expression in cells, and ultimately gene expression is controlled by the macromolecular interactions between regulatory proteins and DNA. The NASA Critical Path Roadmap identifies "Muscle Alterations and Atrophy" and "Radiation Effects" as Very Serious Risks and Severe Risks, respectively, in long term space flights.

The specific problem addressed by Dr. Young's research ("Skeletal Muscle Atrophy and Muscle Cell Signaling") is that skeletal muscle loss in space cannot be prevented by vigorous exercise. Aerobic skeletal muscles (i.e., red muscles) undergo the most extensive atrophy during long-term space flight. Of the many different potential avenues for preventing muscle atrophy, Dr. Young has chosen to study the β-adrenergic receptor (βAR) pathway. The reason for this choice is that a family of compounds called βAR agonists will preferentially cause an increase in muscle mass of aerobic muscles (i.e., red muscle) in animals, potentially providing a specific pharmacological solution to muscle loss in microgravity. In addition, muscle atrophy is a widespread medical problem in neuromuscular diseases, spinal cord injury, lack of exercise, aging, and any disease requiring prolonged bedridden status. Skeletal muscle cells in cell culture are utilized as a model system to study this problem.

Dr. Richmond's research ("Radiation & Cancer Biology of Mammary Cells in Culture") is directed toward developing a laboratory model for use in risk assessment of cancer caused by space radiation. This research is unique because a human model will be developed utilizing human mammary cells that are highly susceptible to tumor development. This approach is preferential over using animal cells because of problems in comparing radiation-induced cancers between humans and animals.

For further information, see the presentations made by Dr. Ronald Young and Dr. Robert Richmond in Appendix C, page B-13.

2.3.4 Growth Defects in Biomacromolecular Crystals

NASA's ground based program confirmed close similarity between protein and small molecules crystal growth, but also revealed essential differences.

No understanding exists as to why and when crystals grown in space are, in ≈20 percent of cases, of higher quality. More rationale is needed in flight experiments.

Ferritin crystals grown in space are ≈2.5 times cleaner than their terrestrial counterparts. This may occur because of the existence of a zone depleted with respect to impurities around a crystal growing in stagnant solution. This zone should appear since the distribution coefficient for homologous impurities exceeds unity. This impurity depletion zone hypothesis requires verification and development. Thorough purification from homologous impurities brought about resolution improvement from 2.6 to 1.8Å for ferritin and from 2.6 to 2.0Å for canavalin.

See Dr. Alexander Chernov's presentation and attached text, "Biomacromolecular Crystallization" in Appendix C, page B-30, for more details and view on the NASA biocrystallization program.

2.3.5 New Directions in Biotechnology

The macromolecule crystallization program within NASA is undergoing considerable pressure, particularly budgetary pressure. While it has shown some successes, they have not lived up to the expectations of others, and technological advances may rapidly overtake the natural advantages offered by crystallization in microgravity. Concomitant with the microgravity effort has been a research program to study the macromolecule crystallization process. It was believed that a better understanding of the process would lead to growth of improved crystals for X-ray diffraction studies. The results of the various research efforts have been impressive in improving our understanding of macromolecule crystallization, but have not led to any improved structures. Macromolecule crystallization for structure determination is "one of", the job being unique for every protein and finished once a structure is obtained. However, the knowledge gained is not lost, but instead lays the foundation for developments in new areas of biotechnology and nanotechnology. In this it is highly analogous to studies into small molecule crystallization, the results of which have led to our present day microelectronics-based society. We are conducting preliminary experiments into areas such as designed macromolecule crystals, macromolecule-inorganic hybrid structures, and macromolecule-based nanotechnology. In addition, our protein crystallization studies are now being directed more towards industrial and new approaches to membrane protein crystallization.

For further information, see the presentation made by Dr. Marc Pusey in Appendix C, page B-53.

2.3.6 The Building Blocks of Materials: Gathering Knowledge at the Molecular Level

Two start-up positions were created within SD46 to pursue developments in the rapidly expanding areas of biomineralization and nano-technology. As envisioned by Dr. Sandor Lehoczy, the new laboratories to be developed must have the capacity to investigate not only processes associated with the self-assembly of molecules but also the examination of self-assembled structures. For these purposes, laboratories capable of performing the intended function, particularly light scattering spectroscopy and atomic force microscopy were created. What follows then are recent advances arising from the development of these new laboratories. With the implementation of the Atomic Force Microscopy Facility, examples of investigations that determine a correlation between the molecular structure of materials and their macroscopic physical properties are provided. In addition, examples of investigations with particular emphasis on the physical properties of protein crystals, at the molecular level, and subsequent macroscopic characteristics are as provided. Finally, progress in fabrication of technology at the nano-scale levels at the developmental stage is also presented.

For further information, see the presentation made by Dr. Sridhar Gorti in Appendix C, page B-59.

2.3.7 New Programs Utilizing Light Scattering and Flow Imaging Techniques for Macromolecular Crystal Growth and Fluid Dynamics Studies

Dr. Phil Segre, a physicist by training, is a recent addition to the Biotech group, SD46, having joined NASA in August of 2000. Over the past two years he has been developing a laboratory for the study of macromolecular and protein crystal growth. The main apparatus for this work is a Dynamic Light Scattering apparatus, DLS, which is capable of making highly precise measurements of size distributions of both protein solutions and protein crystals. With Drs. Chernov and Thomas (USRA), he has begun a collaboration studying the affects of protein impurities on protein crystal growth and subsequent crystal quality. One of the hypotheses behind the differences between Earth and space grown protein crystals is that the absorption of harmful impurities is reduced in space due to the absence of convective flows. Using DLS measurements we are examining crystal growth with varying amounts of impurities and testing whether there is a strong physical basis behind this hypothesis. With Dr. Joe Ng of UAH he has been collaborating on a project to examine the folding/unfolding dynamics of large RNA complexes. A detailed understanding of this process is necessary for the handling of RNA in biotech applications, and the DLS instrument gives details and results beyond that of other instruments. With Prof. Jim McClymer of the University of Maine (summer faculty visitor to NASA in 2001, 2002), we have been studying the crystallization process in model colloidal suspensions whose behavior in some cases can mimic that of much smaller protein solutions. An understanding of the self-assembly of colloids is the first step in the process of engineering novel materials for photonic and light switching applications. Finally, he has begun an investigation into the physics of particle sedimentation. In addition to the DLS instrument he also has an instrument (called PIV) that can measure flow fields of fluids. The applications are to the dynamics of protein crystal motions both on earth and in low-gravity.

For further information, see the presentation made by Dr. Phil Segre in Appendix C, page B-69.

2.3.8 Biotechnology Protein Expression and Purification Facility

The purpose of the Project Scientist Core Facility is to provide purified proteins, both recombinant and natural, to the Biotechnology Science Team Project Scientists and the NRA-Structural Biology Test Investigators. Having a core facility for this purpose obviates the need for each scientist to develop the necessary expertise and equipment for molecular biology, protein expression, and protein purification. Because of this, they are able to focus their energies as well as their funding on the crystallization and structure determination of their target proteins.

For further information, see the presentation made by Dr. Laurel Karr in Appendix C, page B-79.

Appendix A

Biological and Physical Science for Exploration Team

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Effect of Viscosity on the Crystallization of Undercooled Liquids

Edwin C. Ethridge SD46

There have been numerous low-g studies of glasses, indicating that low gravity processing enhances glass formation. NASA PI's are investigating the effect of low-g processing on the nucleation and crystal growth rates. Dr Ethridge is investigating a potential mechanism for glass crystallization involving shear thinning of liquids in 1-g. For shear thinning liquids, low-g (low convection) processing will enhance glass formation. The study of the viscosity of glass forming substances at low shear rates is important to understand these new crystallization mechanisms.

The temperature dependence of viscosity of undercooled liquids is also very important for NASA's containerless processing studies. In general, the viscosity of undercooled liquids is not known, yet knowledge of viscosity is required for crystallization calculations. Many researchers have used the Turnbull equation in error. Subsequent nucleation and crystallization calculations can be in error by many orders of magnitude. This demonstrates the requirement for better methods for interpolating and extrapolating the viscosity of undercooled liquids.

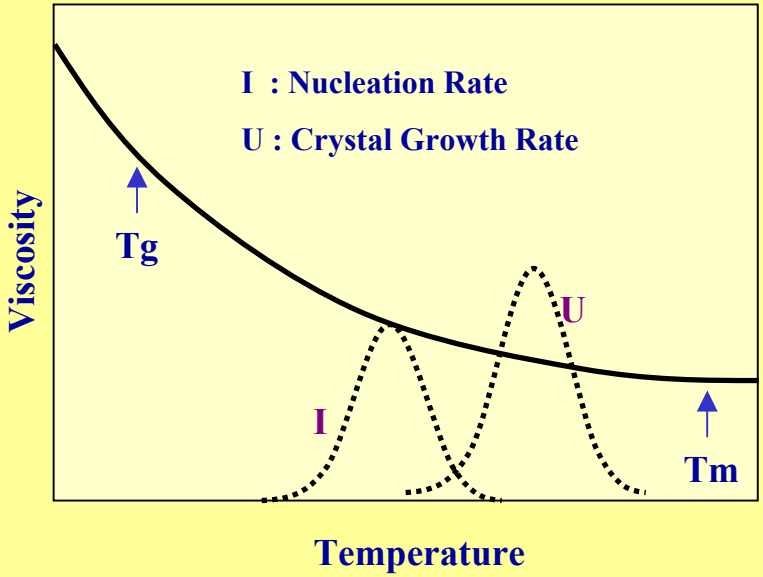
This is also true for undercooled water. Since amorphous water ice is the predominant form of water in the universe, astrophysicists have modeled the crystallization of amorphous water ice with viscosity relations that may be in error by 5 orders of magnitude.

KINETICS OF NUCLEATION AND CRYSTAL GROWTH IN GLASS FORMING MELTS IN MICROGRAVITY

PI Dr Delbert E. Day, U. of Missouri, Rolla

Project Scientist Edwin Ethridge, SD46

Why is there enhanced glass formation in low-g?



Governing Equations

Both are proportional to $1 / \eta$

$$I = (kTn_V/3pl^3\eta)\exp(-W^*/kT)$$

$$U = (fkT/3pl^2\eta)[1-\exp(-V_m\Delta G_V/RT)]$$

Neither equation contains a gravity term

Unexplained Enhanced Glass Formation in low-g

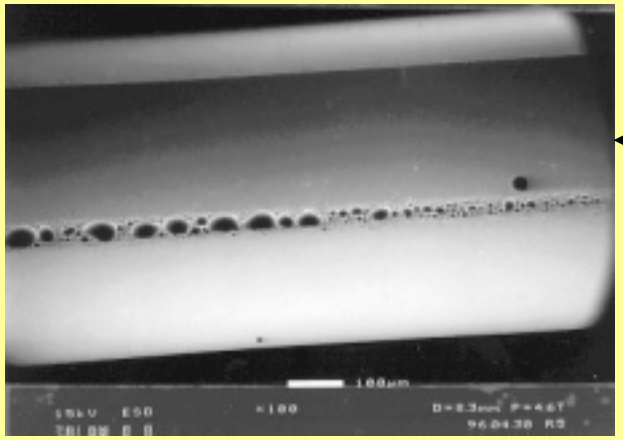
C Barta et al J Non-Cry Solids 35&36:1239 (1980)
G T Petrovskii et al, Steklo I Keramika 1:5 (1983)
D E Day and C S Ray Proc. Mat. Res Soc 87:239 (1987)
S Varma et al Proc. Spacebound 91:248 (1991)
D E Day and C S Ray, Proc 19th Int. Symp. Space Tech. & Sci pp651 (1994)
D S Tucker et al Proc 18th Int Cong Glass (1998)

Mechanisms for the Crystallization of ZBLAN
NASA HQ Ground Based NRA

PI Dr. Edwin C. Ethridge, SD46
Dennis Tucker, SD71 & William Kaukler, UAH

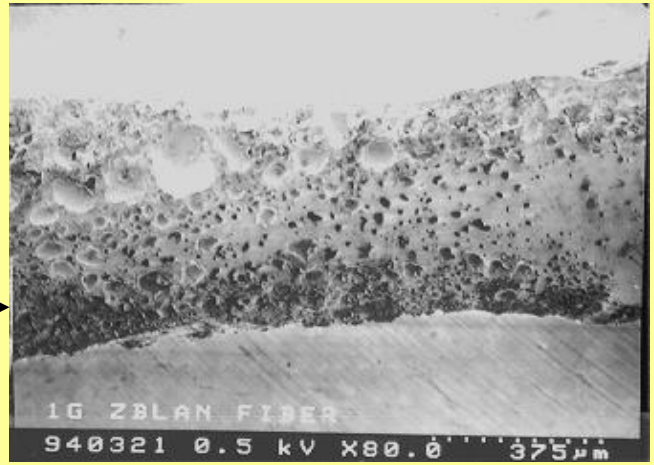
ZBLAN fluoride glass optical fibers exhibit much less tendency to crystallize in low-g than in 1-g on Earth.

This investigation is examining the effects of shear on the viscosity of undercooled glass melts and the subsequent effect on the crystallization of glasses.



ZBLAN fiber heated in a low-g rocket experiment. Essentially no crystallization.

ZBLAN fiber heated in on Earth. Extensive crystallization of the fiber.



ZBLAN is a potential information fiber optical material that suffers from extrinsic signal attenuation caused by crystal nuclei.

Finding a way to better control and eliminate these nuclei could have a very significant impact on the billion dollar information fiber optic industry.

Mechanisms for the Crystallization of ZBLAN NASA HQ Ground Based NRA

PI Dr. Edwin C. Ethridge, SD46

Understanding Enhanced Glass Formation based on Shear Thinning of Glass

- **Shear Thinning is the reduction of viscosity when a fluid flows**

- **Hypothesis:** ***Shear thinning in undercooled liquids increases the rate of nucleation and crystallization of glass forming melts. Shear of the melt can be reduced in low-g enhancing undercooling and glass formation.***

- **Viscosity can be expressed as a function of shear rate**

$$\eta = \eta(\varepsilon)$$

$$I = (kTn_V/3pl^3\,\eta(\varepsilon))\exp(-W^*/kT)$$

$$U = (fkT/3pl^2\eta(\varepsilon))[1-\exp(-V_m\Delta G_V/RT)]$$

- **Fluids exhibit much lower flow rates in low-g than in 1-g**

- **If shear thinning occurs, then the viscosity will be higher in low-g than in 1-g**

"To say that this proposal represents a nontraditional view of nucleation during glass formation is an understatement… and… has identified a possible mechanism to explain the observations … in microgravity." Peer Review comments, *1999.*

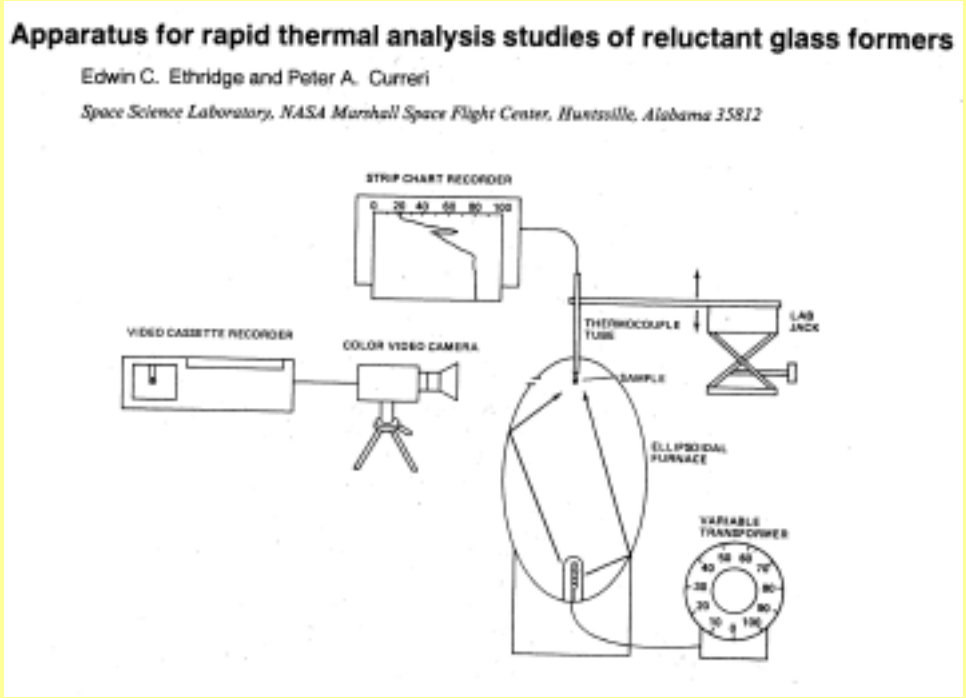
Mechanisms for the Crystallization of ZBLAN NASA HQ Ground Based NRA

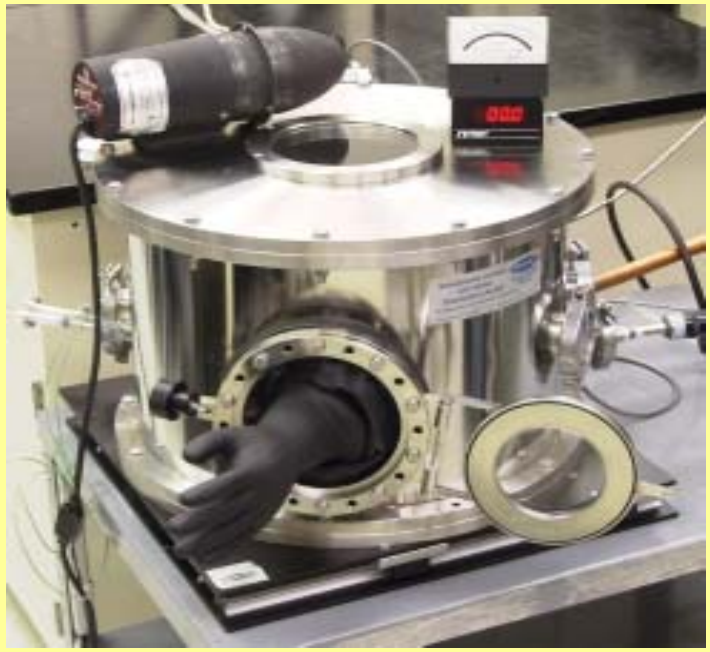
PI Dr. Edwin C. Ethridge, SD46

Dennis Tucker, SD71 & William Kaukler, UAH

Experimental Setup for Nucleation and Crystallization Studies of ZBLAN

A vacuum glovebox has been setup to perform crystallization studies of ZBLAN under very high purity atmospheric control.
Experiments will be performed with samples under shear stress, in order to determine the effect of shear on nucleation and crystallization.





Samples will be rapidly heated and quenched utilizing an ellipsoidal furnace in order to determine the time, temperature, transformation boundary and the critical cooling rate. A system developed a decade ago has been automated with Lab View computer control and data acquisition.

Mechanisms for the Crystallization of ZBLAN
NASA HQ Ground Based NRA

PI Dr. Edwin C. Ethridge, SD46
Dennis Tucker, SD71 & William Kaukler, UAH

Experimental Studies of Nucleation and Crystallization Studies of Glass

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Heterogeneous-Nucleation and Glass-Formation Studies of $56Ga_2O_3 \cdot 44CaO$

EDWIN C. ETHRIDGE* and PETER A. CURRERI

Space Science Laboratory, NASA Marshall Space Flight Center, Huntsville, Alabama 35812

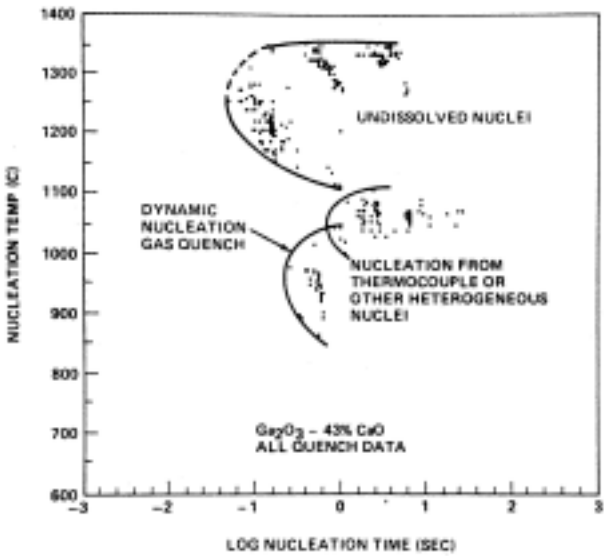
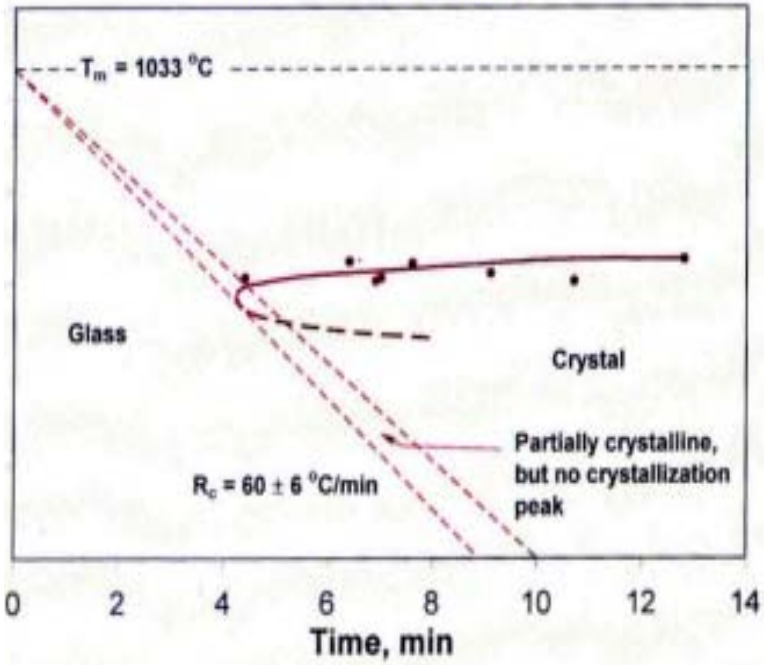


Fig. 5. Plot of nucleation temperature vs log (nucleation time) for all the samples with continuous-cooling-crystallization boundaries drawn for each proposed heterogeneous nucleation mechanism.

Delbert Day (2001)
TTT Diagram for Li_20-SiO_2 Glass
(Continuous Cooling)



Mechanisms for the Crystallization of ZBLAN NASA HQ Ground Based NRA

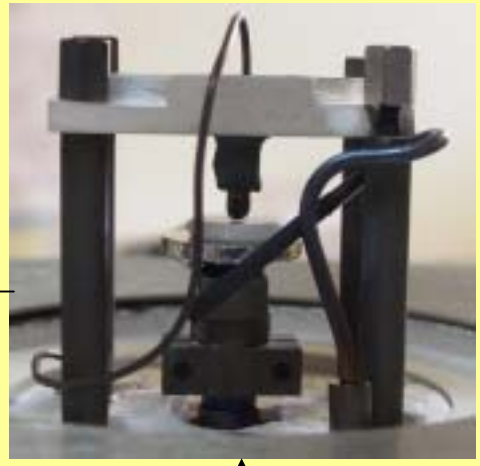
PI Dr. Edwin C. Ethridge, SD46

Dennis Tucker, SD71 & William Kaukler, UAH

Experimental Setup for Shear Dependent Viscosity Measurement

A high temperature Dynamic Mechanical Thermal Analyzer is being redesigned to perform controlled shear and controlled stress experiments on viscous fluids for viscosity measurements.

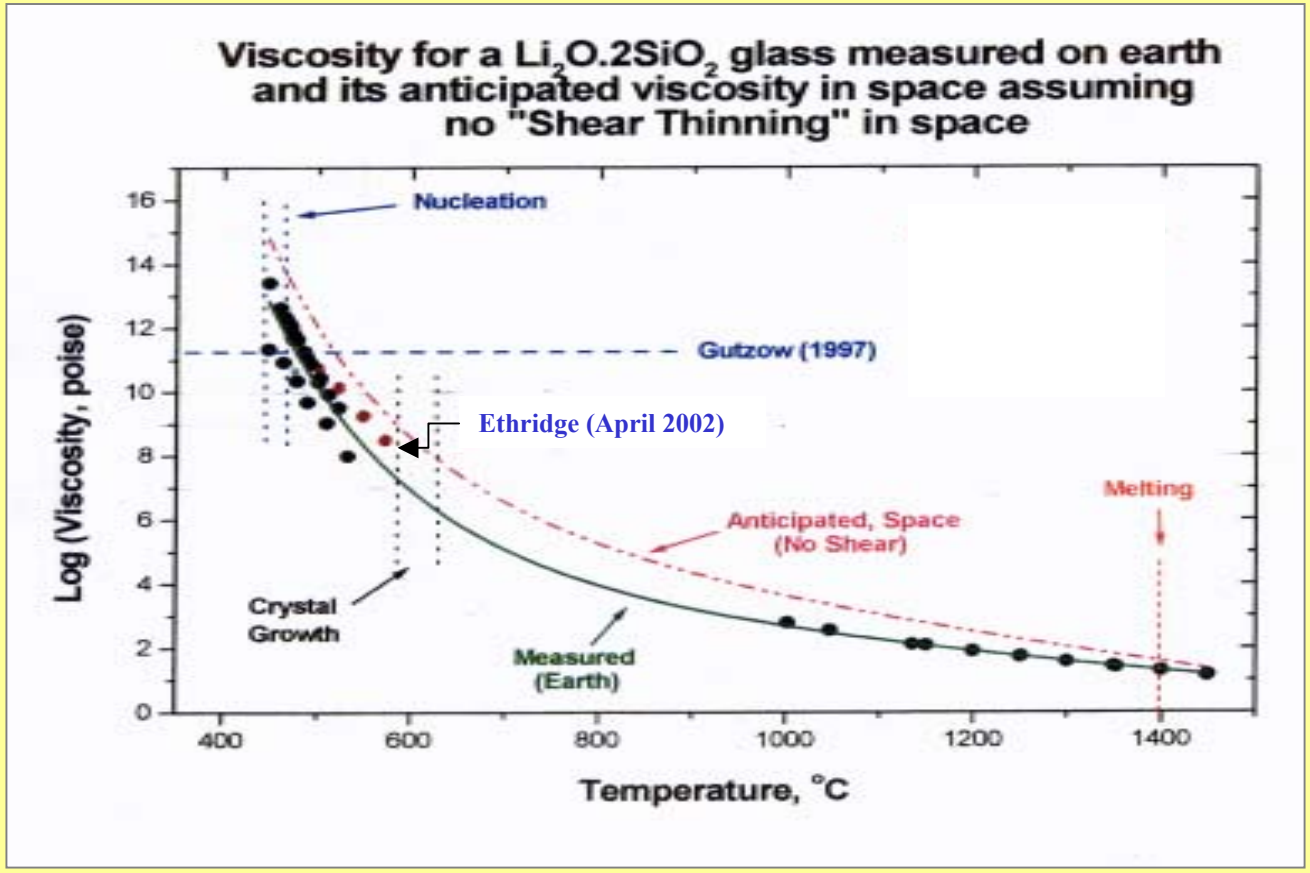
Controlled stress with measured shear experiments are being utilized to determine if glasses exhibit shear thinning. Methods include parallel plate squeeze flow, penetration, fiber pulling, and 3 point beam bending experiments.



Penetration apparatus is illustrated

VISCOSITY OF LITHIUM di-SILICATE GLASS

Edwin Ethridge, SD46 and William Kaukler, UAH



Research Issue

Develop Viscosity Measurement Method for Different Shear Rates

Mathematical Model, Viscosity vs. Shear Rate And Viscosity vs. Temperature for the Method

Perform Critical Experiments And Crystallization Calculations

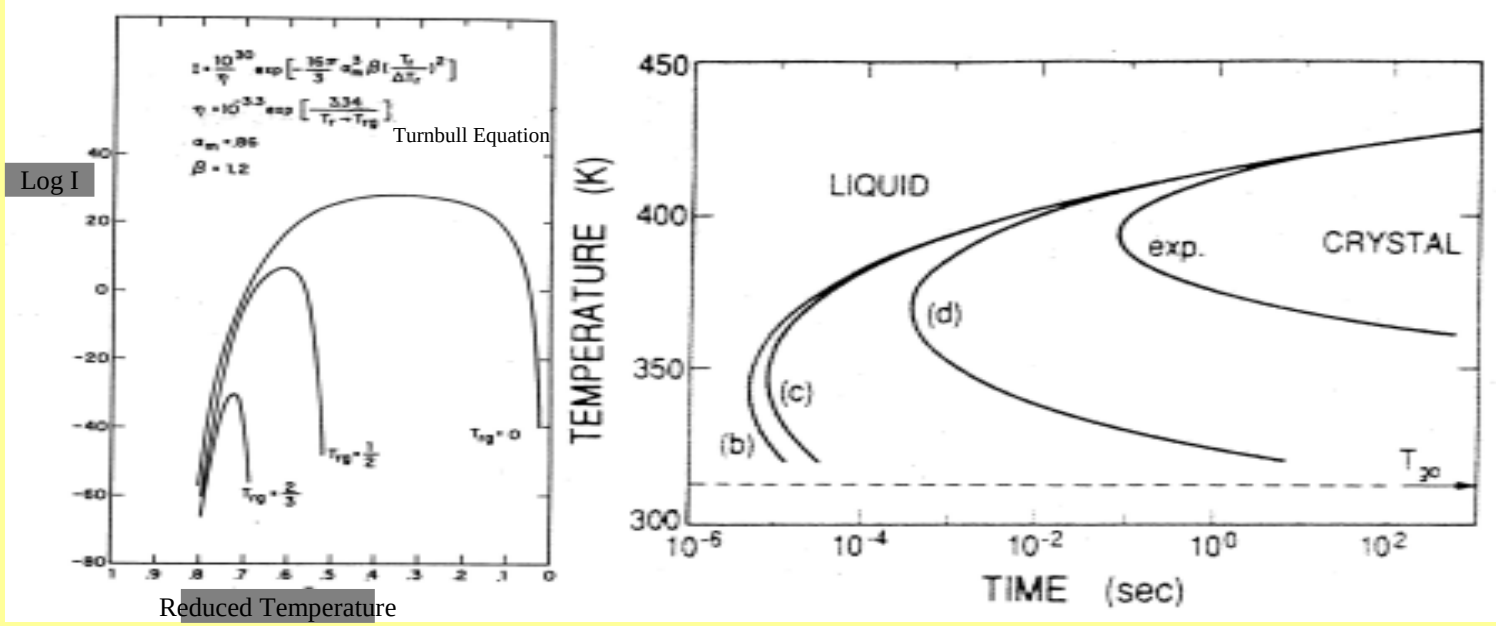
ERRONEOUS MODELING OF THE VISCOSITY OF UNDERCOOLED ALLOYS

Edwin Ethridge, SD46

Studies of undercooled alloys are a very important part of the microgravity program. Calculations of nucleation rate, extent of undercooling and crystallization are dependent on an assumed temperature dependence for the undercooled metallic viscosity.

60 Orders of Magnitude Range Of Nucleation Rate

5 Orders of Magnitude Range, Crystallization and Nucleation Time



"Mis-applications" of Turnbull's Equation: D Turnbull (1969) Contemp Phys 10:473.

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- H J Fecht, J H Perepezko, M C Lee & W L Johnson (1990) J Appl Phys 8:4495
- H J Fecht (1991) Mater Sci & Eng A133:443
- D M Herlach, R F Cochrane, I Egry, H J Fecht & A L Greer (1993) Inter Mater Rev 38:273
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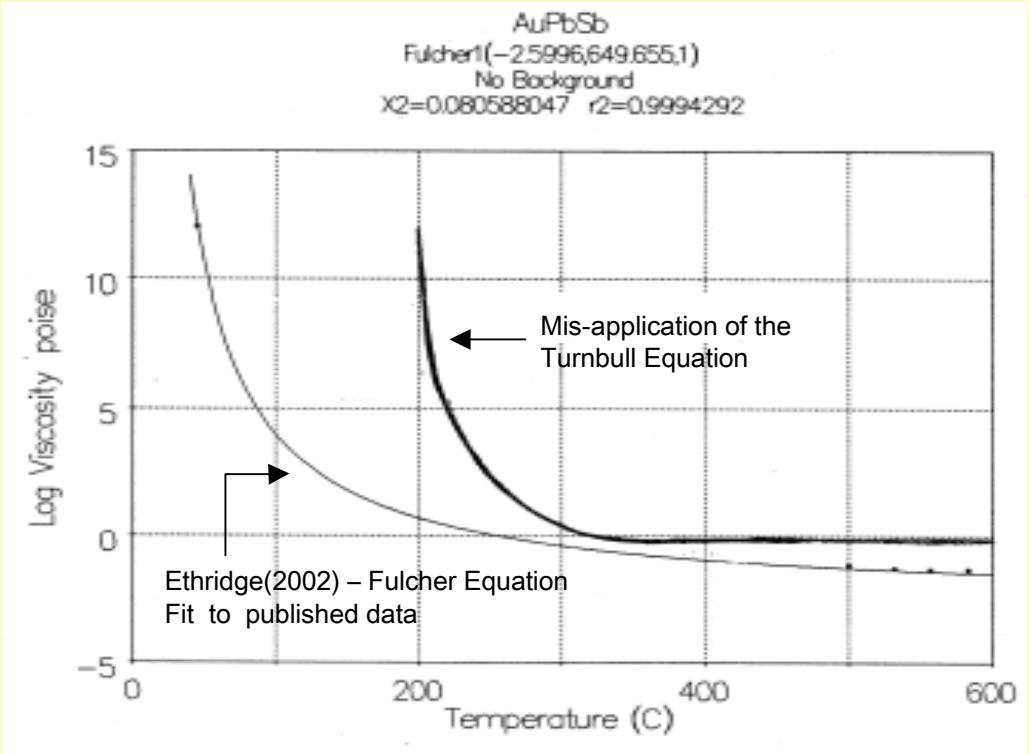
ERRONEOUS MODELING OF THE VISCOSITY OF UNDERCOOLED ALLOYS

Edwin Ethridge, SD46



Research Approach

Measure the Viscosity of Amorphous Samples of Alloys Near the Glass Transition Temperature with DMTA and of The Molten Liquid with the Electro-Static Levitator.

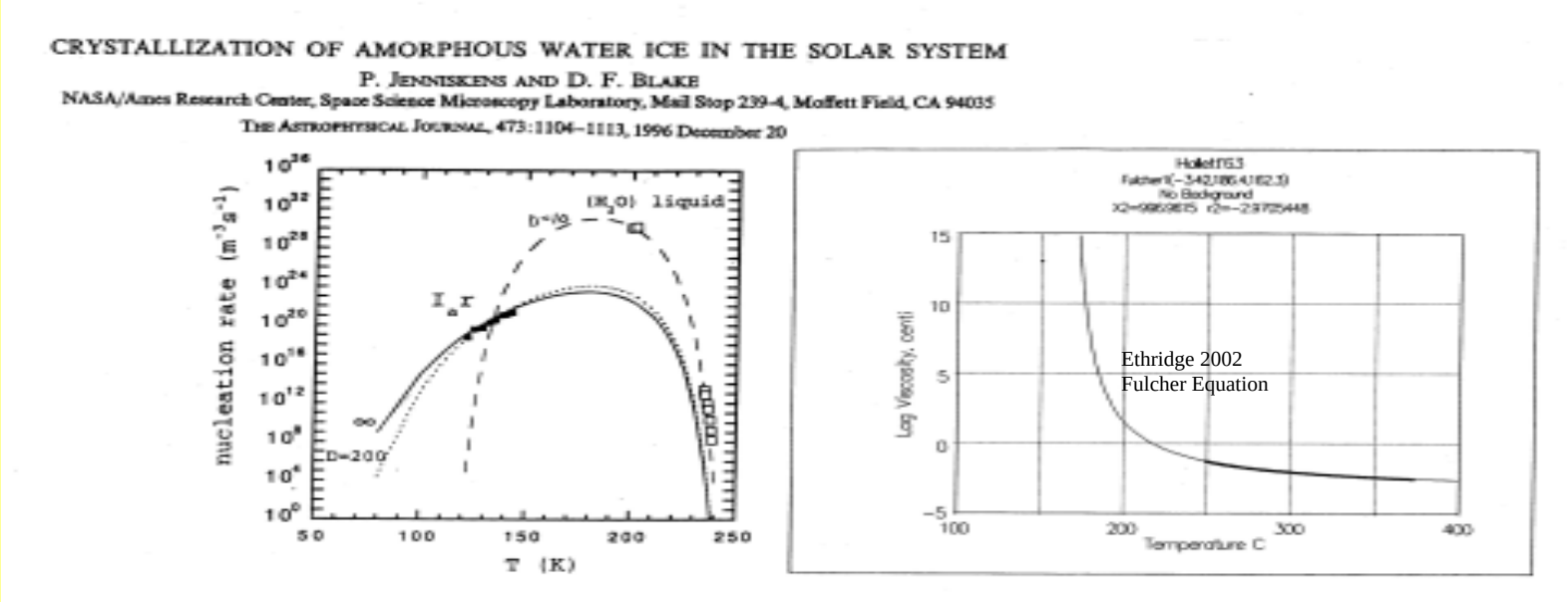
Utilize Various Mathematical Models to Determine Which Best Describes the Undercooled Viscosity

Utilize Interpolated Viscosity Values for Crystallization Calculations

VISCOSITY OF UNDERCOOLED WATER

Edwin Ethridge, SD46

Crystallization of water ice plays an important role in cometary activity. Astrophysical ice is often in the amorphous form. The majority of water in the universe is probably amorphous water.



Research Approach

Vapor Deposit and Measure the Viscosity of Amorphous Water Near the Glass Transition Temperature (100K)

Determine which Mathematical Model Best Describes Undercooled Water

Utilize Interpolated Viscosity Values for Water Crystallization Calculations

"The hope is that if we do understand the ice crystal we shall ultimately understand the glacier." R. P. Feynman (1965)

Surface-Active Biomaterials for Musculo-Skeletal Tissue Culturing

HQ Ground Based NRA Proposal

PI Dr. Edwin C. Ethridge, SD46

Co I Ronald Young, UAH & Ben Penn, SD46

Bioglass is a bio-inspired bone implant material composed of Ca, Na and P in a Silica matrix.

When implanted into bone, bone material is deposited onto the surface and growing bone is deposited onto the glass which becomes totally incorporated into viable bone

Bioglass has the potential to become a bone tissue culture substrate material that can be "engineered" to produce bone tissue responses that mimic low gravity effects.

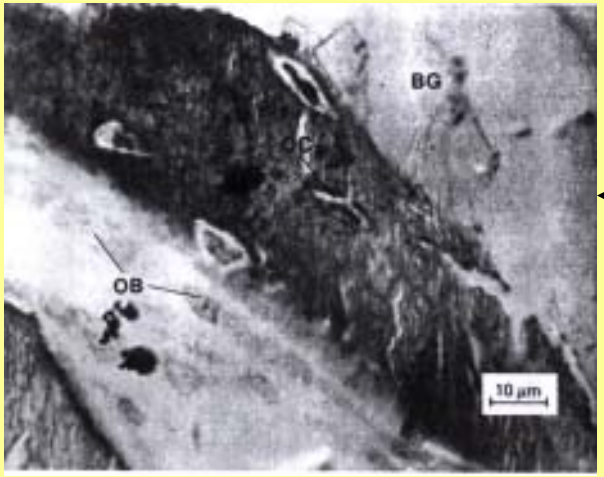
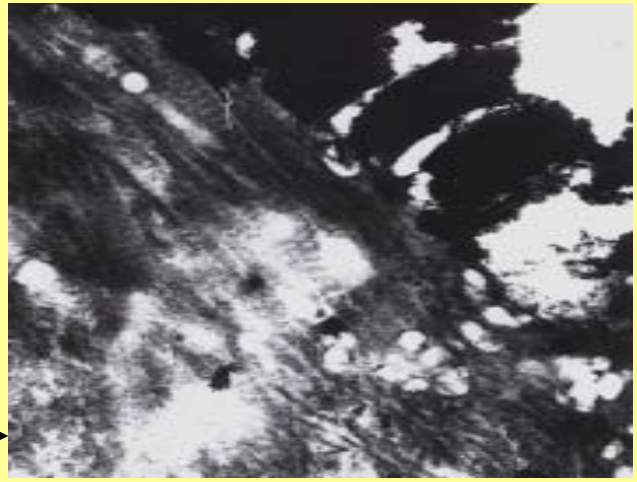


Figure 1. Light-micrograph showing osteocytes (OC) within bone mineral deposited on the surface of bioglass (BG) and osteoblasts (OB) in the growing bone interface a distance from the bioglass surface.

Figure 2. TEM micrograph showing the direct chemical bond between bioglass and bone. Notice the collagen fibers aligned with the bioglass surface.



"*Biomaterials: An Interfacial Approach*", Academic Press, 1982. L.L. Hench and E.C.Ethridge

Surface-Active Biomaterials for Musculo-Skeletal Tissue Culturing

HQ Ground Based NRA Proposal

PI Dr. Edwin C. Ethridge, SD46

Co I Ronald Young, UAH & Ben Penn, SD46

Objectives

1. The primary objective is to develop in-house capability to culture osteoblast cells from a number of sources,

2. To develop the procedures for monitoring the development of the cells through the progression of differentiation, examining the expression of proteins (collagen and osteocalcin), measuring the extracellular matrix, observing the morphology of the actin cytoskeleton, and the total number of cells,

3. To culture osteoblast cells in controlled 1-g conditions of culture flasks and compare with those grown in simulated low-g conditions (i.e. rotary bio-reactor).

4. To utilize a number of biomaterial substrates to examine the differences in cell development with bioceramics having different reactivities.

5. The ultimate goal is to extend previous studies by developing a working model bone tissue culturing system in order to develop macro-molecular strategies to inhibit osteoclastic activity associated with bone loss in low-gravity.

Basic and Applied Materials Science Research Efforts at MSFC Germane to NASA Goals

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Narrative Overview – May 2002

Presently, Dr. Richard N. Grugel is conducting a number of investigations that blend basic research with engineering application in support of NASA goals. They are:

1) "Pore Formation and Mobility (PFMI) – An ISS Glovebox Investigation"
   NASA Selected Project – 400-34-3D
2) "Interactions Between Rotating Bodies"
   CDDF Project – 279-62-00-16
3) "Molybdenum – Rhenium Alloys for Nuclear Fuel Containment"
   TD Collaboration – 800-11-02
4) "Fabrication of Alumina – Metal Composites for Propulsion Components"
   ED Collaboration – 090-50-10
5) "Radiation Shielding for Deep-Space Missions"
   SD Effort
6) "Other Research"

In brief, "Pore Formation and Mobility" is an experiment to be conducted in the ISS Microgravity Science Glovebox that will systematically investigate the development, movement, and interactions of bubbles (porosity) during the controlled directional solidification of a transparent material. In addition to promoting our general knowledge of porosity physics, this work will serve as a guide to future ISS experiments utilizing metal alloys. "Interactions Between Rotating Bodies" is a CDDF sponsored project that is critically examining, through theory and experiment, claims of "new" physics relating to gravity modification and electric field effects. "Molybdenum – Rhenium Alloys for Nuclear Fuel Containment" is a TD collaboration in support nuclear propulsion. Mo-Re alloys are being evaluated and developed for nuclear fuel containment. "Fabrication of Alumina – Metal Composites for Propulsion Components" is an ED collaboration with the intent of increasing strength and decreasing weight of metal engine components through the incorporation of nanometer sized alumina fibers. "Radiation Shielding for Deep-Space Missions" is an SD effort aimed at minimizing the health risk from radiation to human space voyagers; work to date has been primarily programmatic but experiments to develop hydrogen-rich materials for shielding are planned. "Other Research" includes BUNDLE activities (primarily crucible development), vibrational float-zone processing (with Vanderbilt University), use of ultrasonics in materials processing (with UAH), rotational effects on microstructural development, and application of magnetic fields for mixing.

"Pore Formation and Mobility (PFMI) – An ISS Glovebox Investigation"

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Objective(s): Systematically investigate the development, movement, and interactions of bubbles (porosity) during the controlled directional solidification of a transparent material. Guide future ISS experiments utilizing metal alloys. Potential for other studies, e.g., melt back and dendrite interactions.

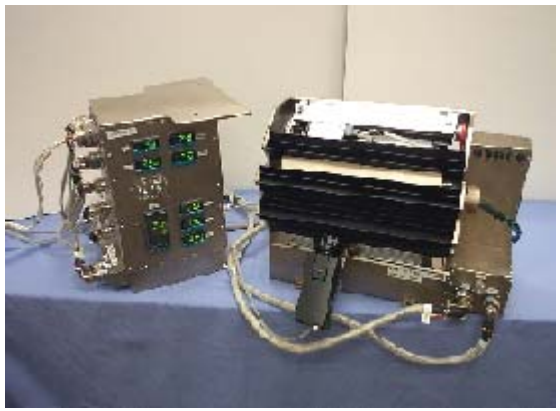
Progress: Flight hardware at KSC, Samples preparation near completion, Delivered to ISS on STS-111 (31 May 2002).

Plans: Continue Ground-based testing.

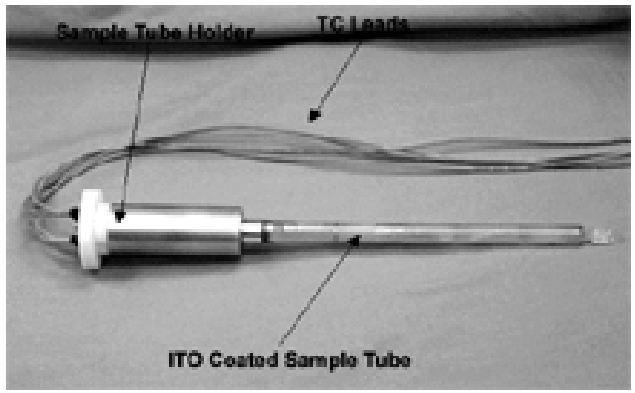
Funding: 400-34-3D

Number of publications resulting from this research to date: 1 publication, 1 proposed, several presentations.

PFMI Controller and Furnace Assembly



Sample and Cartridge



Photographs of the Solid / Liquid interface during Ground Testing

“Interactions Between Rotating Bodies”

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Objective(s): To critically examine, through theory and experiment, claims of “new” physics relating to gravity modification and electric field effects.

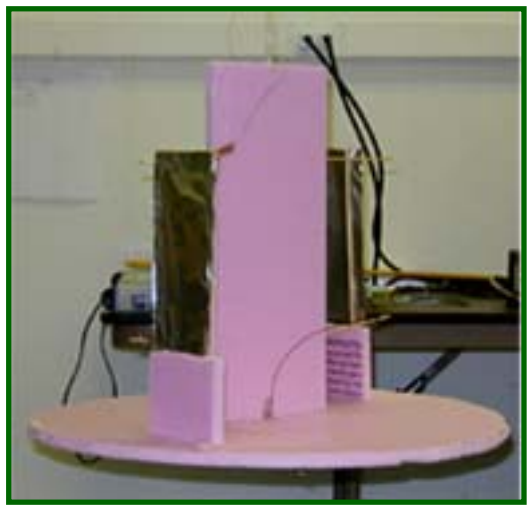
Progress: Hardware has been built and data taken.

Plans: Continue to evaluate data in preparation for submitting publications.

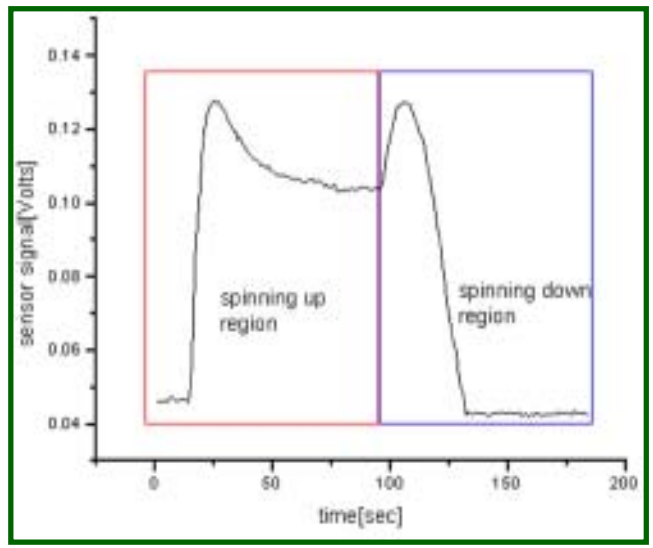
Funding: CDDF 279-62-00-16

Number of publications resulting from this research to date: 2 in progress.

Rotating Mass Device



Electrostatic Accelerator Model



Signal as a Function of Wheel Acceleration

“Molybdenum – Rhenium Alloys for Nuclear Fuel Containment”

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Objective(s): Develop/Evaluate Molybdenum – Rhenium Alloys for use as Containment Tubes for Nuclear Fuel.
Progress: Work began in April 2002, Contacts made with Industry, Material Evaluation beginning.
Plans: Work closely with TD to ensure that Mo-Re product meets or exceeds design specifications.
Funding: 800-11-02
Number of publications resulting from this research to date: None

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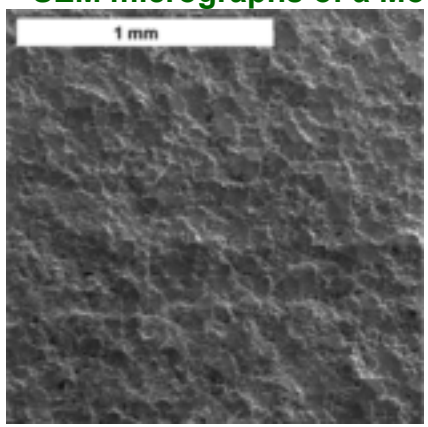
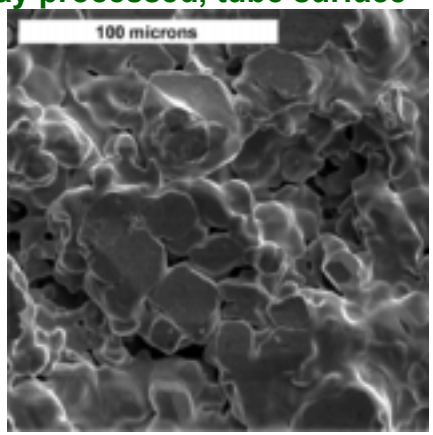
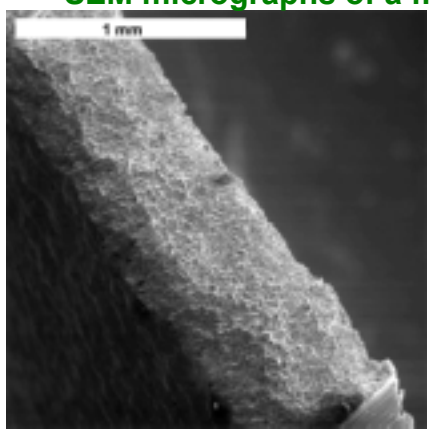
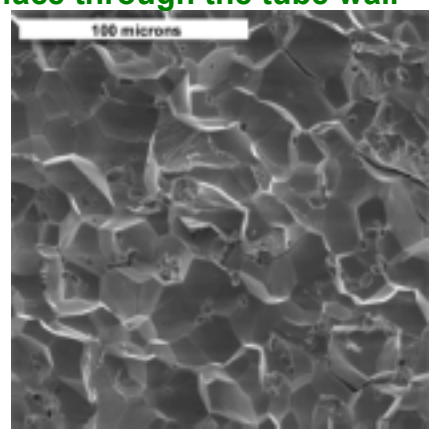
SEM micrographs of a Mo – Re, spray processed, tube surface





SEM micrographs of a fracture surface through the tube wall





“Fabrication of Alumina – Metal Composites for Propulsion Components”

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Objective(s): Increase strength and decrease weight of metal propulsion components through the incorporation nanometer sized alumina fibers.

Progress: Work began in March 2002, Some Material Processing and Evaluations Started.

Plans: Systematically evaluate processing procedures (e.g., compaction, spray processing, laser melting), microstructural examination, and material testing to optimize properties.

Funding: 090-50-10

Number of publications resulting from this research to date: None

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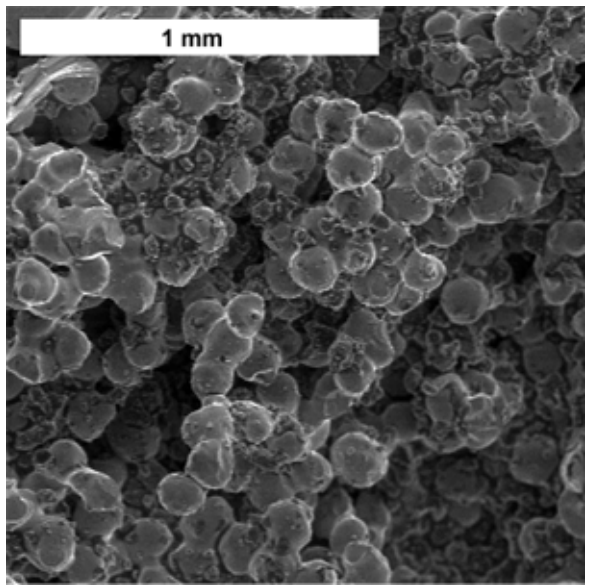
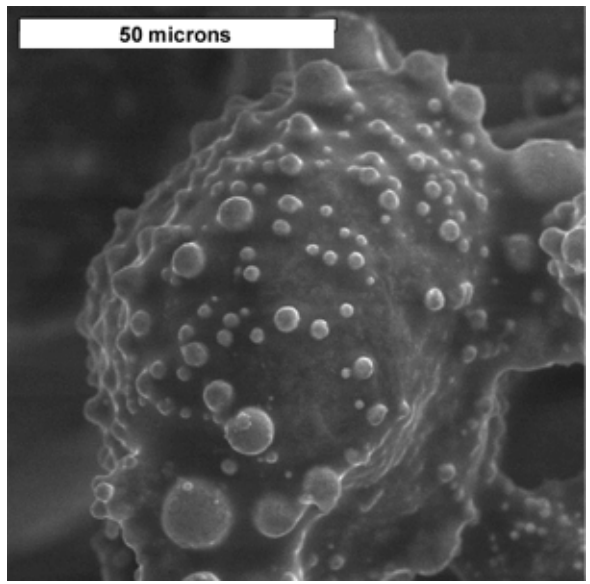
SEM Micrographs of a Compacted 50 Copper – 50 Nickel Powder SampleWith Included Alumina Fibers





"Radiation Shielding for Deep-Space Missions"

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Objective(s): Develop novel, dual-use composite shielding materials to minimizing the health risk to humans from the Galactic Cosmic Ray environment during extended space voyages.

Progress: Fabrication material for Pd-Ag-H alloys obtained, Proposals (1 as PI, 2 as Co-I) sent in response to NASA specific NRA.

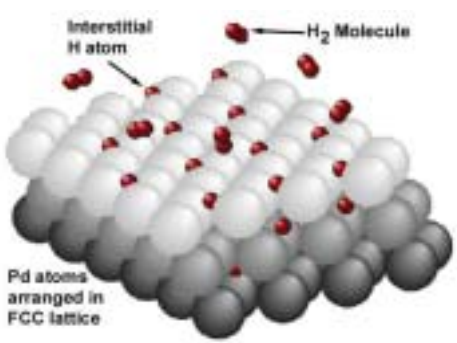
Plans: Fabricate Shielding, Await Proposal results and "Infrastructure" decisions.

Funding: Initial seed money from a TIPs proposal.

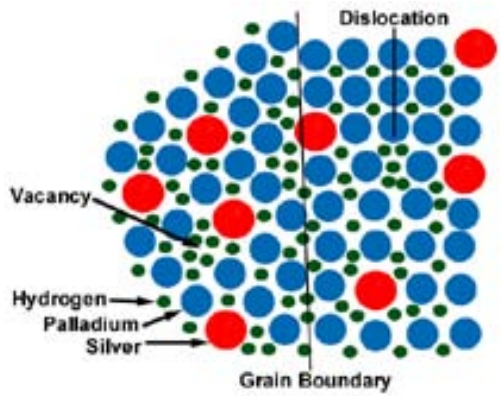
Number of publications resulting from this research to date: Contributions to 2 NASA Workshop Proceedings, Several presentations.

Hydrogen Concentrations in Various Materials

Material	# of H atoms /cm^3 x 10^{22}
Solid Hydrogen (4.2K)	5.3
Water	6.7
Borated Polyethylene	6.1
LiH	5.9
Hydrogen charged Pd	~4.0
H charged Pd-25%Ag	~16 (maybe > 50!)



Hydrogen Dissociation into a Palladium Lattice



Schematic Representation of Hydrogen Diffusing into a Palladium – Silver Lattice

“Other Research”

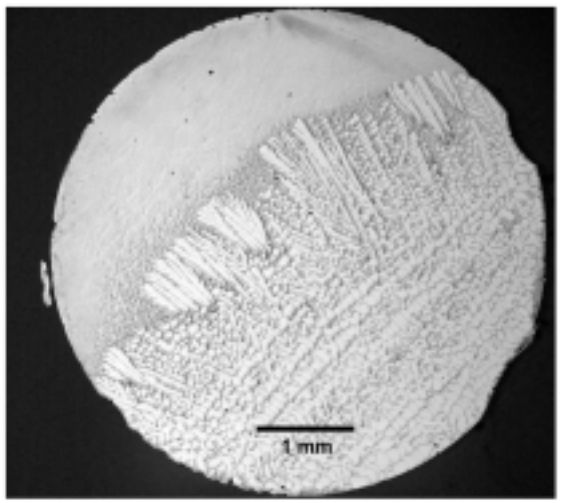
Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

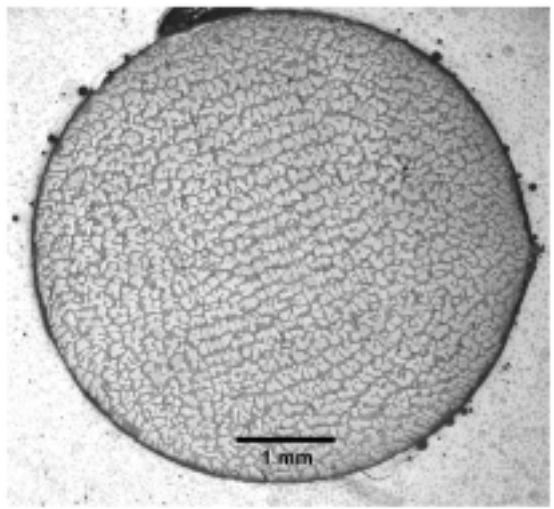
Objective(s): Crucible Development, Improvements to Microstructure through Innovative Processing Techniques.
Progress: Techniques Established.
Plans: Fine Tuning of Procedures, Submit for Additional Funding, Await other Decisions.
Funding: 398-35-10, Residual Project Scientist Funding
Number of publications resulting from this research to date: Many Publications and Presentations, 1 Patent Disclosure

Crucible Design

(Patent Application being filed)

Axial Rotation during Controlled Directional Solidification

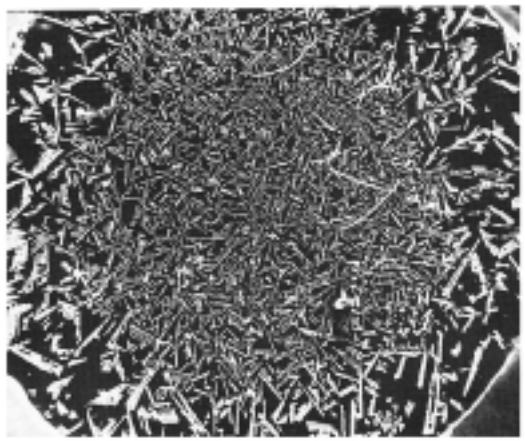


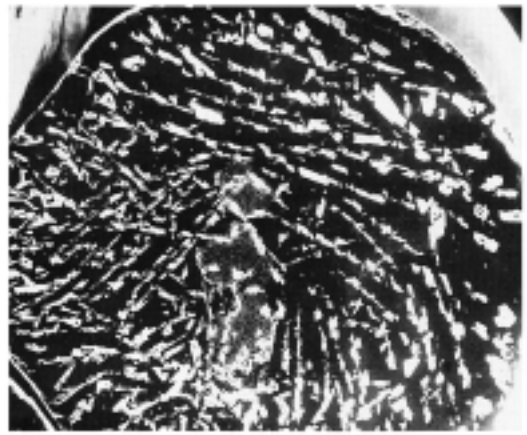


“Other Research -2-”

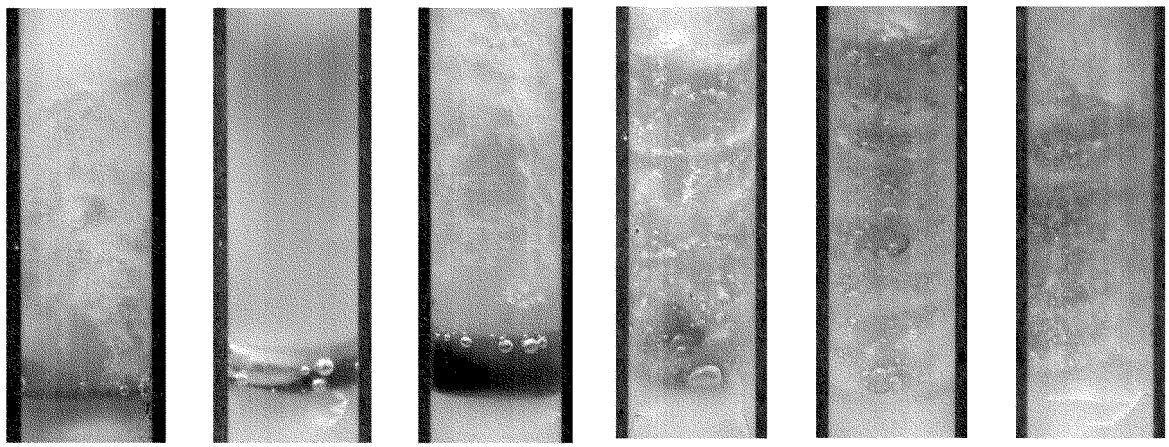
Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Application of Controlled Vibrations during Float-zone Processing





Utilizing Ultrasonic Energy to Promote Uniform Dispersions in Immiscible Alloys

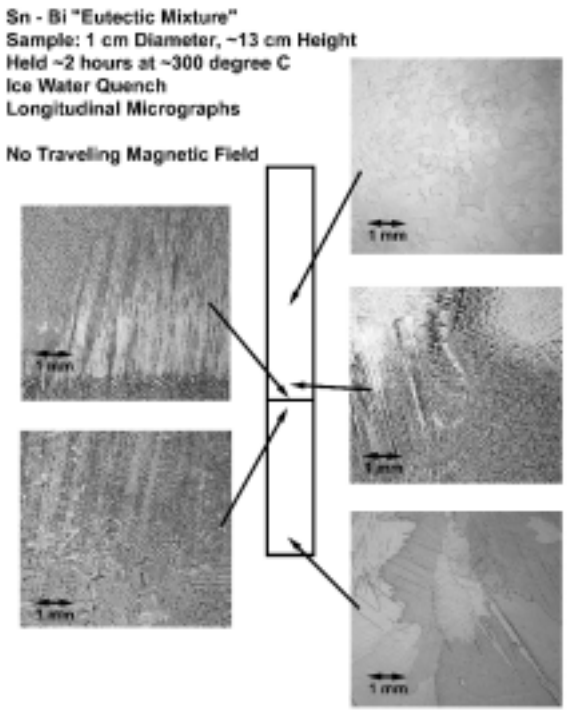


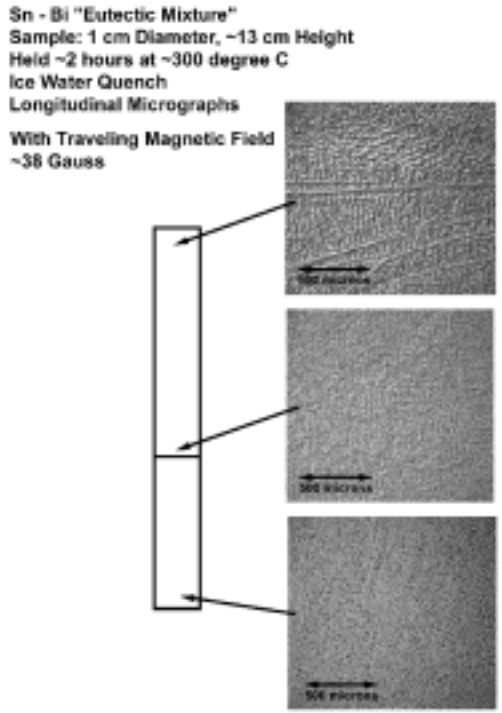
10wt% Glycerol | 15wt% Glycerol | 20wt% Glycerol | Amplitude 64 microns | 101 microns | 137 microns

“Other Research -3-”

Richard N. Grugel – SD46 – Biological & Physical Sciences for Exploration

Application of Traveling Magnetic Fields to Promote Mixing in Alloys (Co-I)





Development of Aerogel Molds for Metal Casting Using Lunar and Martian Regolith

(CDDF Project)

B. Penn/ SD 46, J-A. Gavira-Gallardo, S. Sen/ USRA-SD46, L. Sibille/ USRA-SD 46

ABSTRACT

In the last few years NASA has set new priorities for research and development of technologies necessary to enable long-term presence on the Moon and Mars. Among these key technologies is what is known as In-Situ Resource Utilization, which defines all conceivable usage of mineral, liquid, gaseous, or biological resources on a visited planet. In response to this challenge, we have been focusing on developing and demonstrating the manufacturing of a specific product using Lunar and Martian soil simulants, i.e. a mold for the casting of metal and alloy parts, which will be an indispensable tool for the survival of outposts on the Moon and Mars. In addition, our purpose to demonstrate the feasibility of using mesoporous materials such as aerogels to serve as efficient casting molds for high quality components in propulsion and other aerospace applications.

The first part of the project consists of producing aerogels from the in-situ resources available in Martian and Lunar soil. The approach we are investigating is to use chemical processes to solubilize silicates using organic reagents at low temperatures and then use these as precursors in the formation of aerogels for the fabrication of metal casting molds. One set of experiments consists of dissolving silica sources in basic ethylene glycol solution to form silicon glycolates. When ground silica aerogel was used as source materials, a clear solution of silicon glycolate was obtained and reacted to form a gel thus proving the feasibility of this approach. However, in the application of this process to Lunar and Martian simulants did not result in the formation of a gel; however, further study is in progress. In the second method acidified alcohol is reacted with the simulants to form silicate esters. Preliminary results indicate the presence of silicon alkoxide in the product distillation. However, no gel has been obtained so further characterization is ongoing.

In the second part of the project, the focus has been on developing a series of aerogel plates suitable for thin plate metal casting and ingot metal castings. The influence of aerogels on thin wall metal castings was studied by placing aerogel plates into the cavities of thin sections of resin bonded sand molds. An A1 based commercial alloy (A356) containing 7°/o Si was poured into these molds. Post-solidification studies provide evidence that aerogel inserts significantly reduce the cooling rate during solidification. The advantage of a lower rate using aerogel inserts was reflected in the reduction of casting defects such as shrinkage porosity. Quantitative results support the hypothesis that using aerogels as a mold material can offer definite advantages when used as casting thin sections.

As a separate effort silica aerogel with cylindrical cavities have been prepared and will be evaluated for casting commercial alloys.

Center Director's Discretionary Fund Project

Development of Aerogel Molds for Metal Castings Using Lunar and Martian Regolith

Principal Investigator: Dr. Benjamin Penn/ SD 46

Co-Investigators: Dr. Jose A. Gavira-Gallardo/ UAH

Dr. Subhayu Sen/ USRA-SD46

Dr. Laurent Sibille/ USRA-SD46

OBJECTIVES

1. Replace Welded parts with cast components in propulsion engines to increase durability by 10-20 missions between overhauls.

- **Problem:**
  Propulsion components consist of thin wall sections in which there are high solidification rates which cause casting defects.
- **Solution:**
  Insert thin Aerogel plates in sand Molds. These will lower the solidification rate thus producing a sound casting.

2. Develop molds for casting high temperature alloys needed to improve propulsion performance.

- **Problem:**
  Directional solidification required for components such as turbine blades are labor intensive and expensive.
- **Solution:**
  Develop Aerogel molds with bottom chill plate in which there are low radial heat transfer that will induce directional solidification.

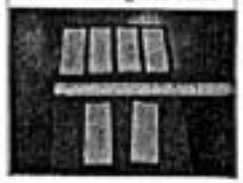
3. Produce silica-based materials such as glasses, ceramics, Aerogels, and coatings from Lunar and Martian soil simulants.

- **Problem:**
  Existing processes for Silica extraction involve the use of dangerous reagents at high temperatures. These include the use of acids and silicate melts.
- **Solution:**
  Use low temperature dissolution of silicates in organic solvents in combination with the sol-gel process.

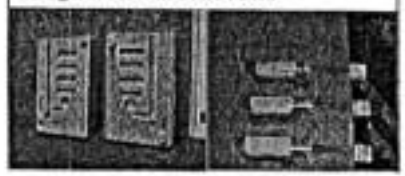
ACHIEVEMENTS

☐ Thin Wall Casting With Aerogel Inserts

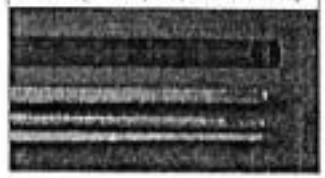
Silica Aerogel Inserts



Aerogel Inserts in Sand Mold



Castings Made With Aerogel Inserts (t = 2.5, 3.5, and 6.0 mm)

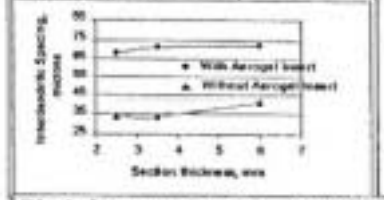


Microstructural Analysis

With Aerogel inserts, slower cooling rate and hence coarser structure. (50X)

Without Aerogel inserts, faster cooling rate and hence finer structure (50X)

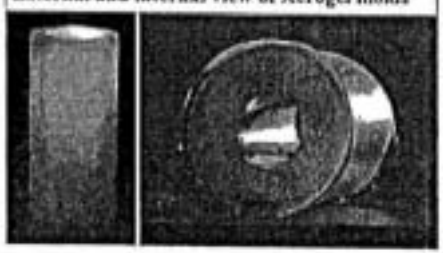
Quantitative Analysis



Shrinkage porosity decreases by 27% when Aerogel inserts were used

☐ Directional Solidification Using Aerogel Mold

External and internal view of Aerogel molds

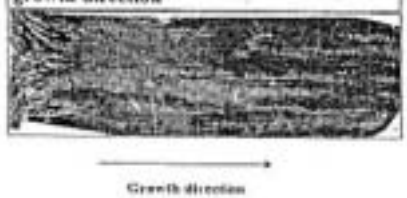


Al-Cu alloy casting

Aerogel mould was used for 4 consecutive castings

Al-Cu alloy cast in Aerogel mold

Microstructure shows directionality in growth direction



Low Temperature Dissolution of Silica from Soils

Work at MSFC

Soluble Silica Gel precursors obtained from:

- ✓ Dissolution of Calcium silicate in HCl/Ethanol-Toluene
- ✓ Dissolution of Silica Aerogel in Ethylene Glycol

Outside related work

Research on dissolution of silica (sand, quartz) in organic solvents (Laine, U. Michigan; Goodwin, Case Western)

Importance to NASA / MSFC

New silica extraction technology developed in-house will support NASA's strategy for Space Resource Utilization at planetary outposts in Solar System

Propulsion Parts Casting in Aerogel Molds

Work at MSFC

- ✓ Cast a full scale turbine blade in Aerogel mold
- ✓ $Zr0_2$, $Ti0_2$Aerogel molds for casting high temperature propulsion alloys
- ✓ Use infra-red CCD system for real time imaging of metal solidification in Aerogel molds
- ✓ Modeling of microstructure evolution in castings using temperature data

Outside related work

Dr. L. Ratke, Institute for Space Simulation
DLR, Germany

- ✓ Development of a furnace with Aerogel walls for in-orbit processing (ARTEMIS)
- ✓ Research on investment castings in silica Aerogel molds

Importance to NASA / MSFC

In-house effort is focused on demonstrating new casting techniques for high performance materials needed in propulsion systems

FUTURE WORK

Proposals

- ✓ **High performance alloy castings in Aerogel molds (US Army / NASA)**
- ✓ **Sol-Gel materials from chemically dissolved silica (DOE, NASA Research Announcement, NSF)**

Collaborations

- ✓ **Properties of propulsion parts cast in Aerogel molds (Propulsion Research Center, MSFC)**

Graphite/ Ultra-High Modulus Polyethylene Hybrid Fiber Composites with Epoxy and Polyethylene Matrices for Cosmic Radiation Shielding

(Proposal submitted in response to NRA-01-OBPR-05)

B. Penn/SD46, R. Grugel/ SD 46, J. Watts/ SD 50, R. Kaul/ ED 34, A. B. Hulcher/ ED 34, D. Edwards/ ED 31, D. Trinh/ ED 34, A. Hodge/ ED 34

ABSTRACT

One of the most significant technical challenges in long-duration space missions is that of protecting the crew from harmful radiation. Protection against such radiation on a manned Mars mission will be of vital importance both during transit and while on the surface of the planet. The development of multifunctional materials that serve as integral structural members of the space vehicle and provide the necessary radiation shielding for the crew would be both mission enabling and cost effective. Additionally, combining shielding and structure could reduce total vehicle mass. Hybrid laminated composite materials having both ultra-modulus polyethylene (PE) and graphite fibers in epoxy and PE matrices could meet such mission requirements. PE fibers have excellent physical properties, including the highest specific strength of any known fiber. Moreover, the high hydrogen content of polyethylene makes the material an excellent shielding material for cosmic radiation. When such materials are incorporated into an epoxy or PE matrix a very effective shielding material is expected. Boron may be added to the matrix resin or used as a coating to further increase the shielding effectiveness due to boron's ability to slow thermal neutrons. These materials may also serve as micrometeorites shields due to PE's high impact energy absorption properties. It should b noted that such materials can be fabricated by existing equipment and methods. It is the objective of this work therefore to: (a) perform preliminary analysis of the radiation transport within these materials; (b) fabricate panels for mechanical property testing before and after radiation exposure. Preliminary determination on the effectiveness of the combinations of material components on both shielding and structural efficiency will be made.

Proposal Submitted in Response to NRA-01-OBPR-05

Graphite/Polyethylene Hybrid Fiber Reinforced Composites with Epoxy and Polyethylene Matrices for Cosmic Radiation Shielding

Principal Investigator: Benjamin Penn/ SD 46

Co-Investigators: Richard Grugel/ SD 46

John Watts/ SD 50

Raj Kaul/ ED 34

A.B. Hulcher/ ED 34

David Edwards/ ED 31

Diep Trinh/ ED 34

A. Hodge/ ED 34

Objectives and Technical Approach

- **Develop cost and mission effective multifunctional graphite/ultra-high modulus polyethylene (PE) hybrid fiber reinforced composites for cosmic radiation shielding. These materials will also serve as a structural material and may also provide protection from micrometeorites.**

- **Initially predict the suitability of these materials for cosmic radiation shielding using NASA radiation transport codes.**

- **Fabricate panels of the best candidates and expose them to radiation levels and temperatures that will be encountered during transit and while on the surface of Mars.**

- **Add boron to some of these composites as particles and/or coatings and determine the efficiency of these materials in absorbing low energy neutron.**

- **Determine the mechanical properties before and after exposure to the desired temperatures and radiation levels.**

Significance of Using These Materials for Cosmic Radiation Shielding

- These composites are low cost and mission effective and will be prepared using readily available materials and existing manufacturing processes.

- They will be lightweight, safe and flight ready since the components are PE, epoxies and graphite.

- The use of ultra-high modulus polyethylene fibers in these composites provides additional shielding effectiveness and/or improvements in the mechanical properties. The high impact energy absorption of these PE fibers may contribute to protection from micrometeorites.

Experimental Methods

1. Composite Fabrication

- Purchase materials from commercial sources. These include epoxies, PE and graphite fibers, boron particles, and low molecular weight polyethylene.
- Composites will be fabricated using varying weight percentages of plies of PE fiber/epoxy, graphite fiber/ epoxy, and PE fiber/polyethylene, PE fiber/ epoxy.
- Standard processes and equipment will be used in composite fabrication that may include hand lay-up/autoclave cure, vacuum bag/oven cure. And vacuum assisted resin transfer molding (VARTM).

2. Preparation of Boron Particulate Matrices and Coatings

- Uniform mixing of resins with boron particles will be achieved using commercial equipment.
- Plies of composites containing boron will be incorporated varying weight percentages. Boron will also be added as a coating on the surface of the fabricated composite materials.

3. Simulations and Testing of Radiation Shielding Effectiveness

- Cosmic radiation shielding effectiveness will be estimated using the High Z Element Transport Code (HZETRN) developed at NASA Langley Research Center.
- Estimates will be checked in cooperation with the team for radiation transport measurement.
- Thermal neutron absorption effectiveness of boron containing composites will be determined using procedures described in the scientific literature. This involves exposing the samples to low energy neutrons from a 5-curie plutonium/beryllium source.

4. Effect of the Space Environment on the Mechanical Properties

- Test panels will be fabricated and exposed to the temperatures and levels of radiation that will be encountered during space travel to Mars.
- Mechanical testing include uni-axial tension and compression, three point bending, and impact testing

Program for the Increased Participation of Minorities in NASA-Related Research

Benjamin G. Penn/ SD 46

ABSTRACT

The goal of this program is to increase the participation of minorities in NASA related research and "Science for the Nation's Interest". Collaborative research projects will be developed involving NASA-MSFC, National Space Science and Technology Center (NSSTC), other government agencies, industries and minority serving institutions (MSIs). The primary focus for the MSIs will be on Alabama A&M University and Tuskegee University, which are in partnership with the NSSTC. These schools have excellent Ph.D. programs in physics and materials science and engineering, respectively. The first phase of this program will be carried out at Alabama A&M University in the "Research and Development Office" in collaboration with Dr. Dorothy Huston, Vice President of Research and Development. The development assignment will be carried out at the NSSTC with Sandy Coleman/ RS01 and this will primarily involve working with Tuskegee University.

A portion of the program will be devoted to identifying and contacting potential funding sources for use in establishing collaborative research projects between NASA-MSFC, other government agencies, NSSTC, industries, and MSIs. These potential funding sources include the National Science Foundation (NSF), National Institute of Health (NIH), Department of Defense (DOD), Army, Navy, and Air Force. Collaborative research projects will be written mostly in the following research areas:

a. Cosmic radiation shielding materials
b. Advanced propulsion material
c. Biomedical materials and biosensors
d. In-situ-resource utilization
e. Photonics for NASA applications

(NASA Administrator's Fellowship Program for 2002)

Program for the Increased Participation of Minorities in NASA-Related Research

Benjamin G. Penn/ SD 46

Professional Development Assignment

1. Alabama A&M University

- "Research and Development Office" in collaboration with Dr. Dorothy Huston, Vice President of Research and Development
- Excellent PhD program in Physics

2. National Space Science and Technology Center (NSSTC)

- Collaboration with Sandy Coleman/ SD03 and Judy Simonds/ SD03
- Assignment will be to work primarily with Tuskegee University which has an excellent PhD program in materials science and engineering
- Efforts will be made to establish joint research projects between Alabama A&M University, Tuskegee University and other minority serving institutions where appropriate

Program Goals

1. Increase the participation of minority serving institutions in NASA-Related Research and "Science for the Nation's Interest"

   - Radiation shielding materials
   - Advanced Propulsion Materials
   - Biomaterials and biosensors
   - In situ resource Utilization
   - Photonics for NASA applications

2. Contact various funding sources for establishing collaborative research projects

   - Joint research projects will involve NASA-MSFC, NSSTC, other government agencies, minority serving institutions, and industries
   - Potential funding sources include NIH, NSF, DOD, Army, Navy and the Air Force

ATD, Solid-Liquid Interface Characterization Hardware

Abstract

Characterizing the solid-liquid interface during directional solidification is key to understanding and improving material properties. The goal of this Advanced Technology Development (ATD) program has been to develop hardware, which will enable real-time characterization of practical materials, such as aluminum alloys, to unprecedented levels. Required measurements include furnace and sample temperature gradients, undercooling at the growing interface, interface shape, or morphology, and furnace translation and sample growth rates (related). These and other parameters are correlated with each other and time. A major challenge was to design and develop all of the necessary hardware to measure the characteristics, nearly simultaneously, in a smaller integral furnace compatible with existing X-ray Transmission Microscopes, XTMs.

Most of the desired goals have been accomplished through three generations of Seebeck furnace brassboards, several varieties of film thermocouple arrays, heaters, thermal modeling of the furnaces, and data acquisition and control (DAC) software. Presentations and publications have resulted from these activities, and proposals to use this hardware for further materials studies have been submitted as sequels to this last year of the ATD.

Palmer N. Peters, PI
Peter A. Curreri, Co-I
William F. Kaukler, Co-I
Subhayu Sen, Co-I
R. Charles Sisk, Co-I
Francis Wang, Co-I

Project Overview

ATD, Solid/Liquid Interface Characterization Hardware

PM – Isabella Kierk – JPL

PI - Palmer N. Peters - MSFC

Co I - Peter A. Curreri - MSFC

Co I - William F. Kaukler - UAH

Co I - Subhayu Sen - USRA

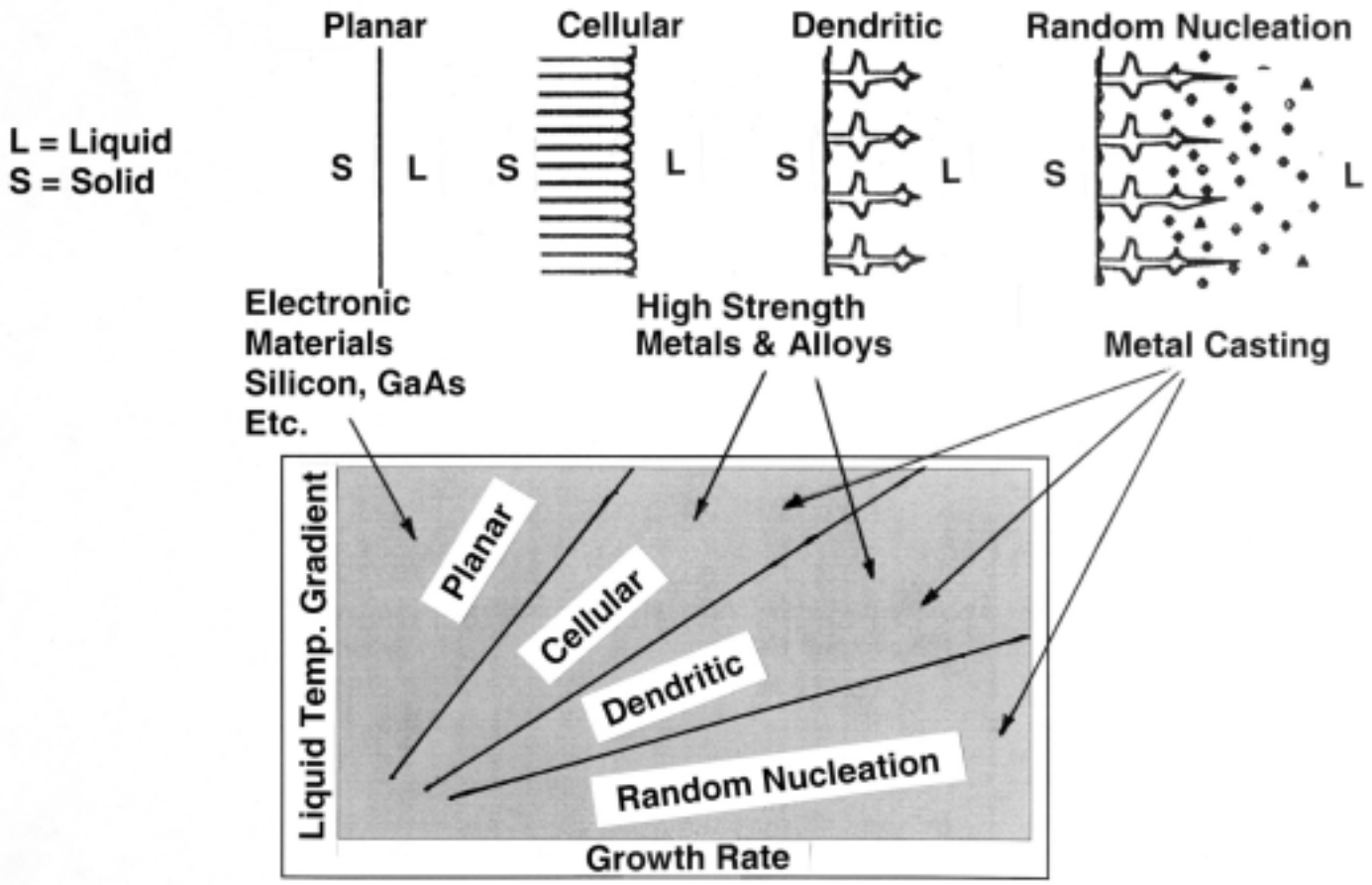
Co I - R. Charles Sisk – MSFC

Co I - Francis Wang – Raytheon

Project Justification

- Characterizing the solid-liquid interface during directional solidification is key to better understanding and control of the properties of materials.
- The morphology of the interface is dependent upon the temperature and velocity of the solidifying interface. Only real-time characterization can provide these measurements.

Changes in Interface Structure During Directional Solidification



Justification (continued)

- Undercooling of the moving interface, compared to a stationary one, is a key parameter to be measured.
- The interface movement (growth rate) and sample temperature gradient are related to, but not exactly equal to, the furnace's translation rate and gradient.
- Time-stamping all measurements in real-time enables cross-correlation of parameters and results.

Background

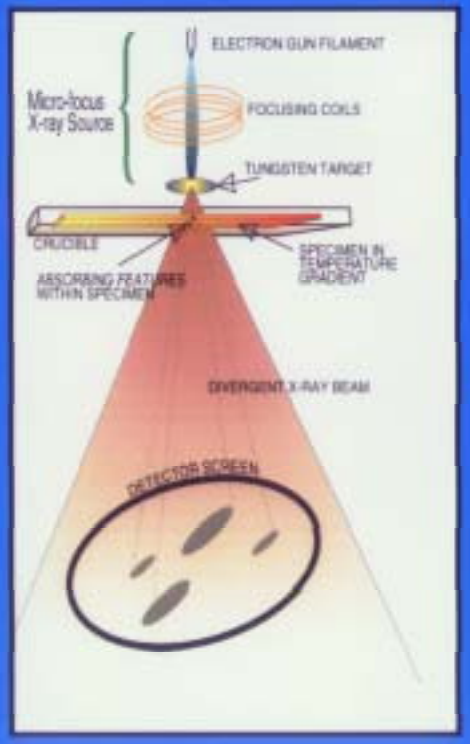
- Seebeck (thermocouple) voltages between a solid and its melt, as junctions, have been used to measure interfacial undercooling. The method fails for non-planar interfaces.
- Typical wire thermocouples interfere with the thermal environment of the interface.
- An array of thermocouples can measure temperature gradients.
- A smaller Seebeck furnace was required to integrate with existing X-ray Transmission Microscopes, XTMs.

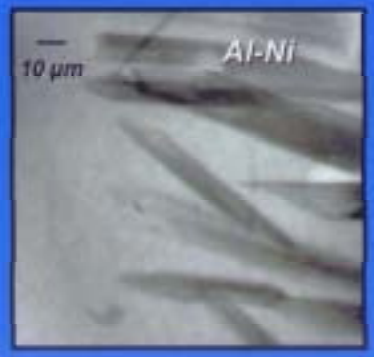
OUTLOOK FOR THE 21st CENTURY

In-Situ Observations of Eutectic Solidification in Metallic Alloys

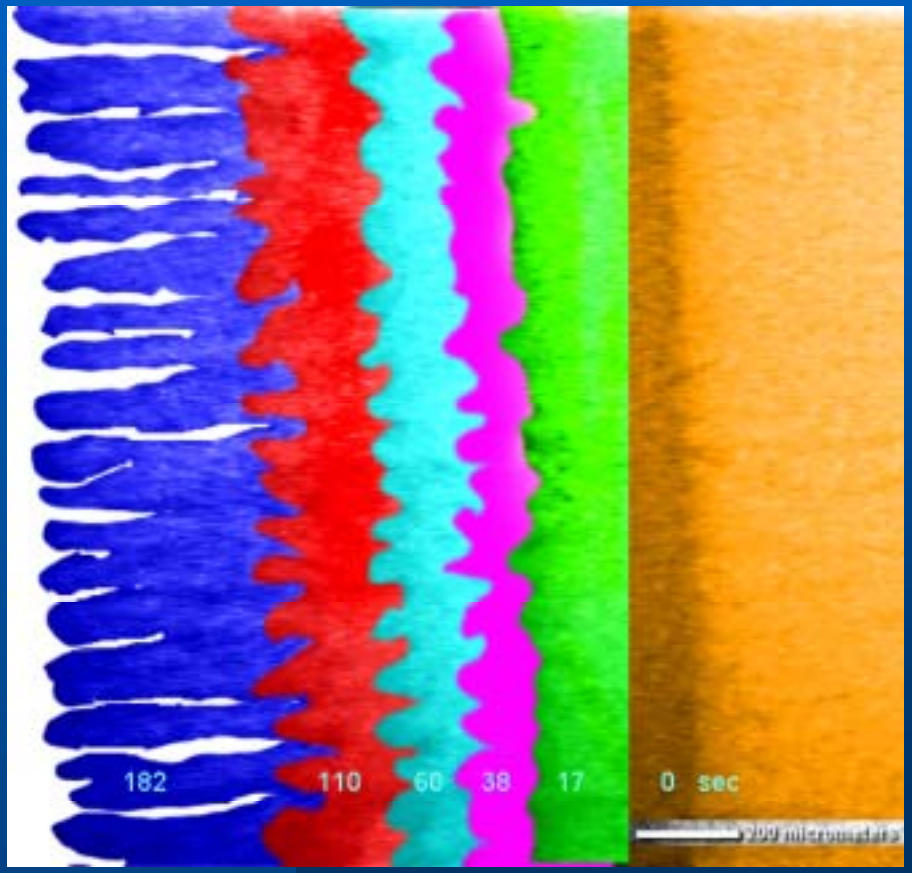
X-ray Transmission Microscope (XTM)

-Kaukler & Curreri





Planar-to-Cellular Transition



- Sequence of XTM radiographs showing planar (right) to cellular (left) interface breakdown [growth from right to left]
- Al-2% Ag alloy
- Gradient 50 °C/cm
- Rate: step up to 3 μm/sec from zero

Technology Developments

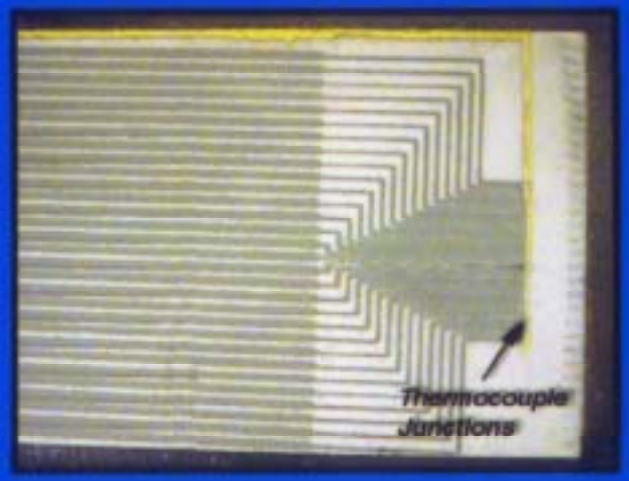
Thermocouple Arrays

- Thin-film micro-arrays were fabricated of conventional K-type materials, but rapidly failed at high temperature.
- Hybrid circuit arrays were fabricated with noble-metal elements and utilized successfully on furnace bore tubes and sample containers.
- Difficulties with adhesion of vacuum deposited noble-metal thin-films were researched and partially solved.
- Thin film arrays, visible in x-ray images for determining position and speed, were developed.
- Protective coatings that stand up to harsh molten aluminum environment have been demonstrated.
- Other array details are available.

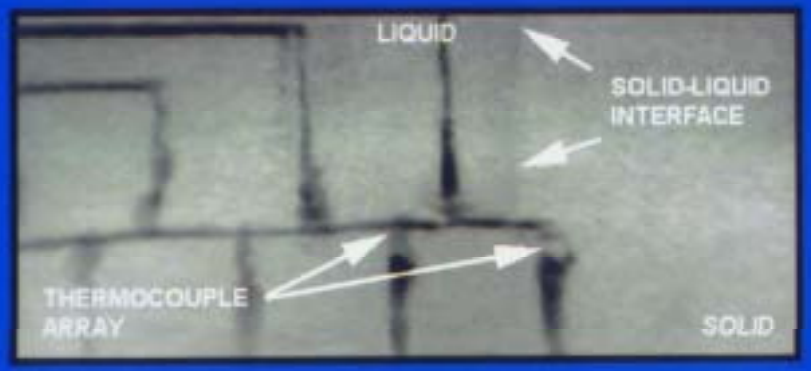
OUTLOOK FOR THE 21st CENTURY

Micro-Thermocouple Arrays to Measure Interface Temperatures

Linear Micro-Thermocouple Array

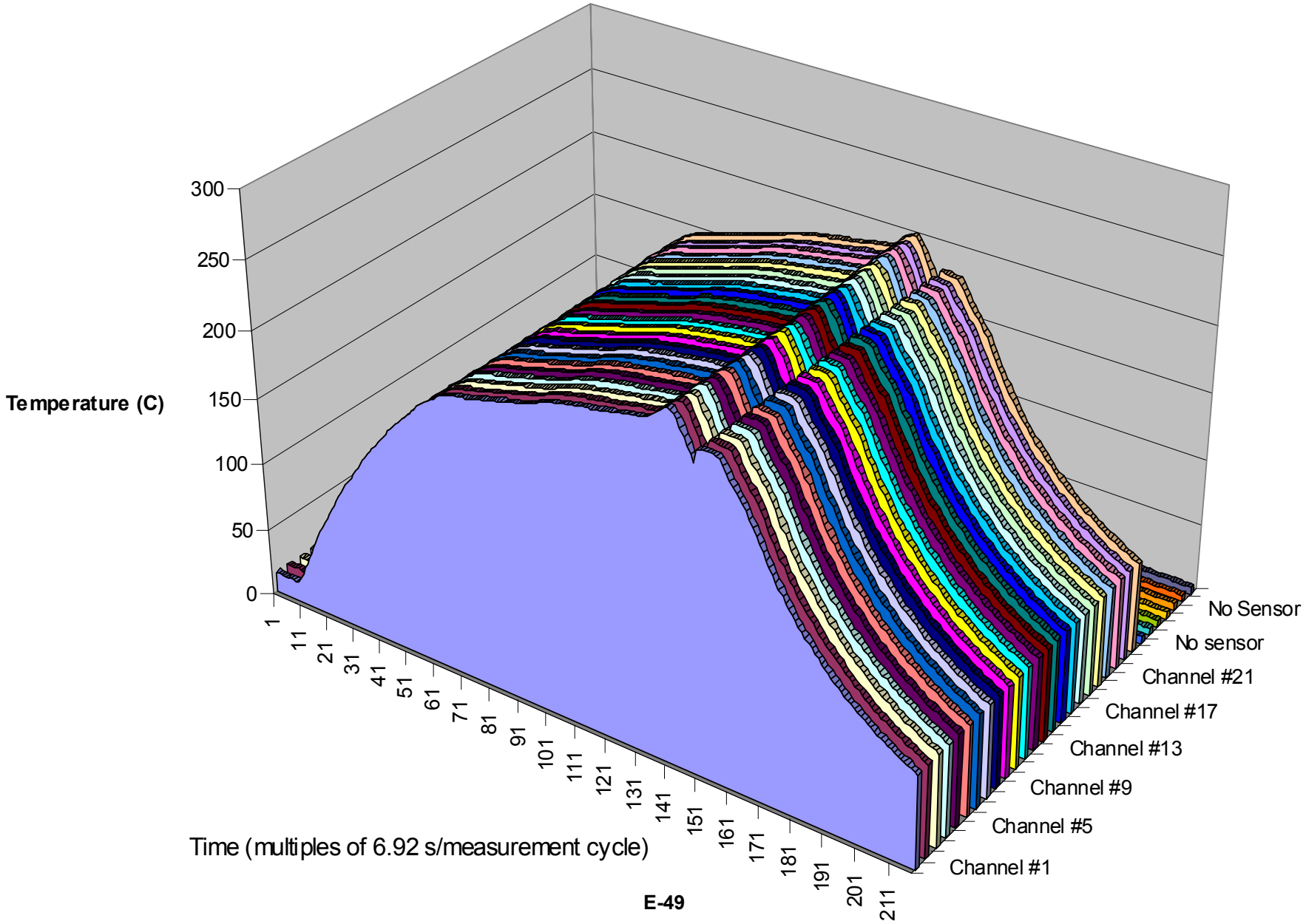


Interface Observations & Micro-Thermocouple Array Using XTM



Courtesy: Palmer Peters, MSFC NASA

Temperature vs. time for 24-thermocouple array in tin.

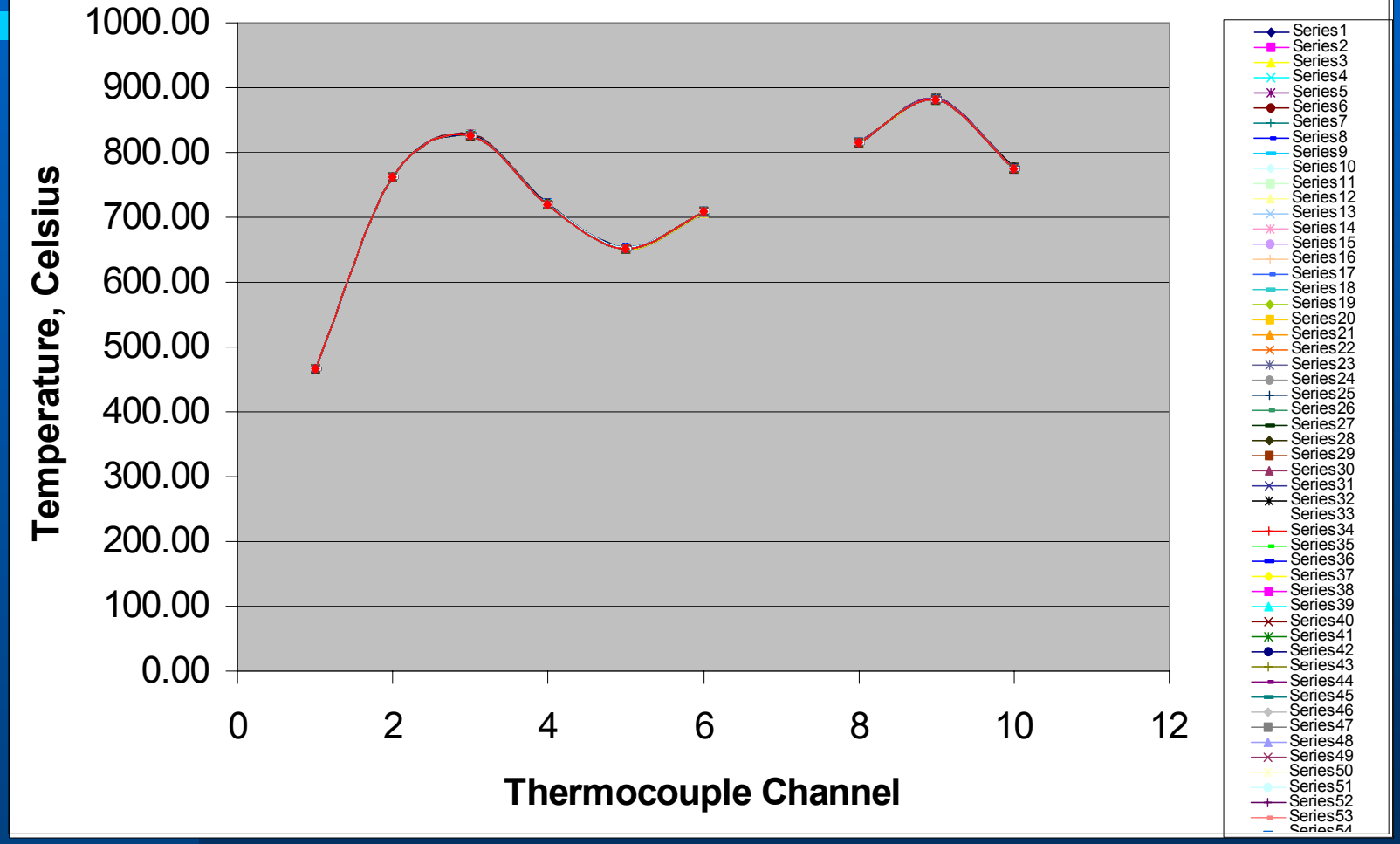


Technology Developments (Continued)

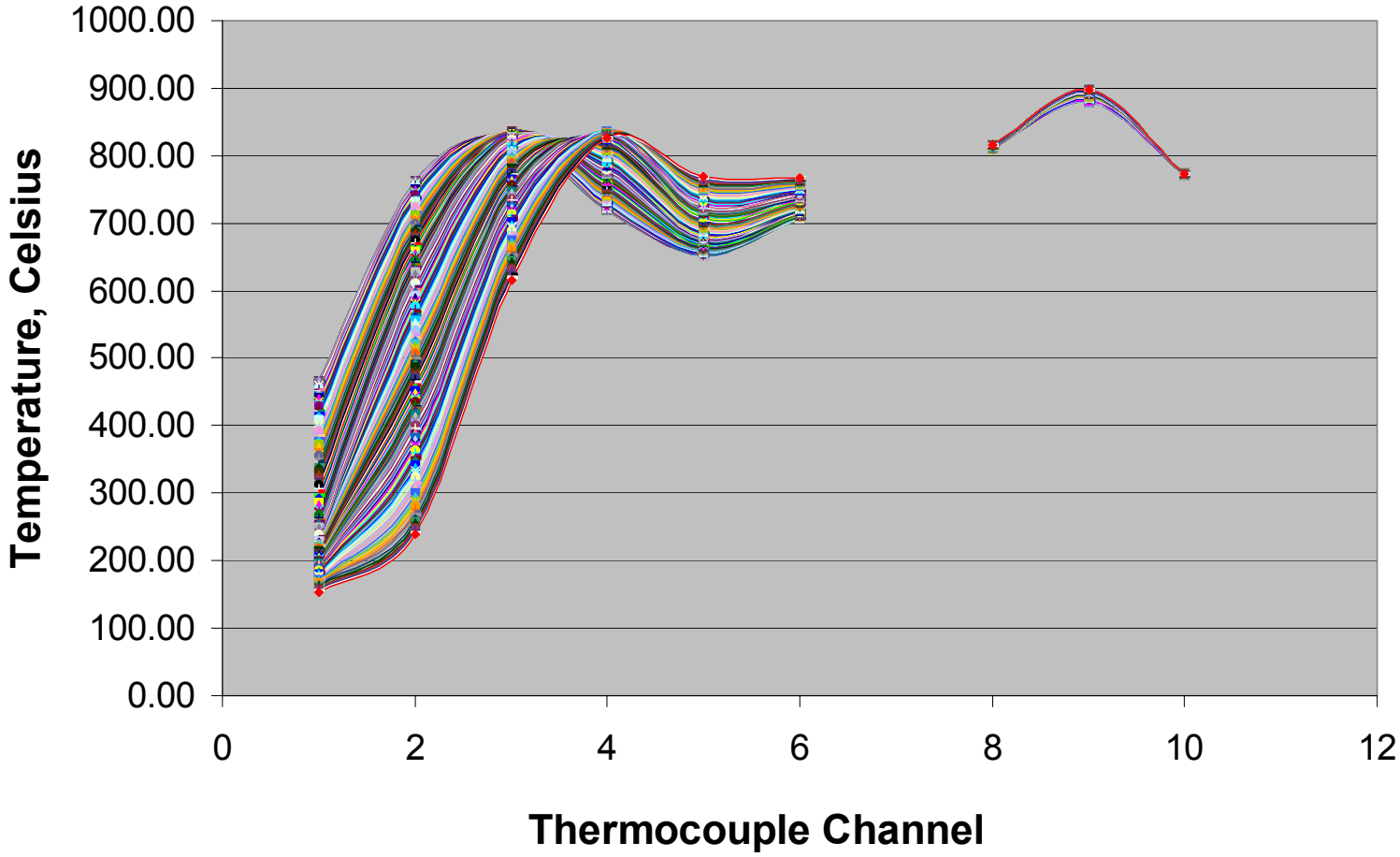
Seebeck Furnaces

- Three generations of furnace were developed.
- First-generation, which was limited to low temperature (<500ºC), verified a compact furnace gave correct results, compared to published data. Some science was obtained using this instrument, resulting in a few papers and presentations.
- Second-generation extended the operating range to at least 1000º C, enabling practical aluminum alloys to be studied while verifying furnace characteristics.
- The last, 3rd-generation, Subcompact Seebeck Furnace, is x-ray transparent, allows higher magnification in XTM, and keeps the moving interface in the field of view of the XTM.

Compact Seebeck Furnace Temperature Profiles, During Steady State

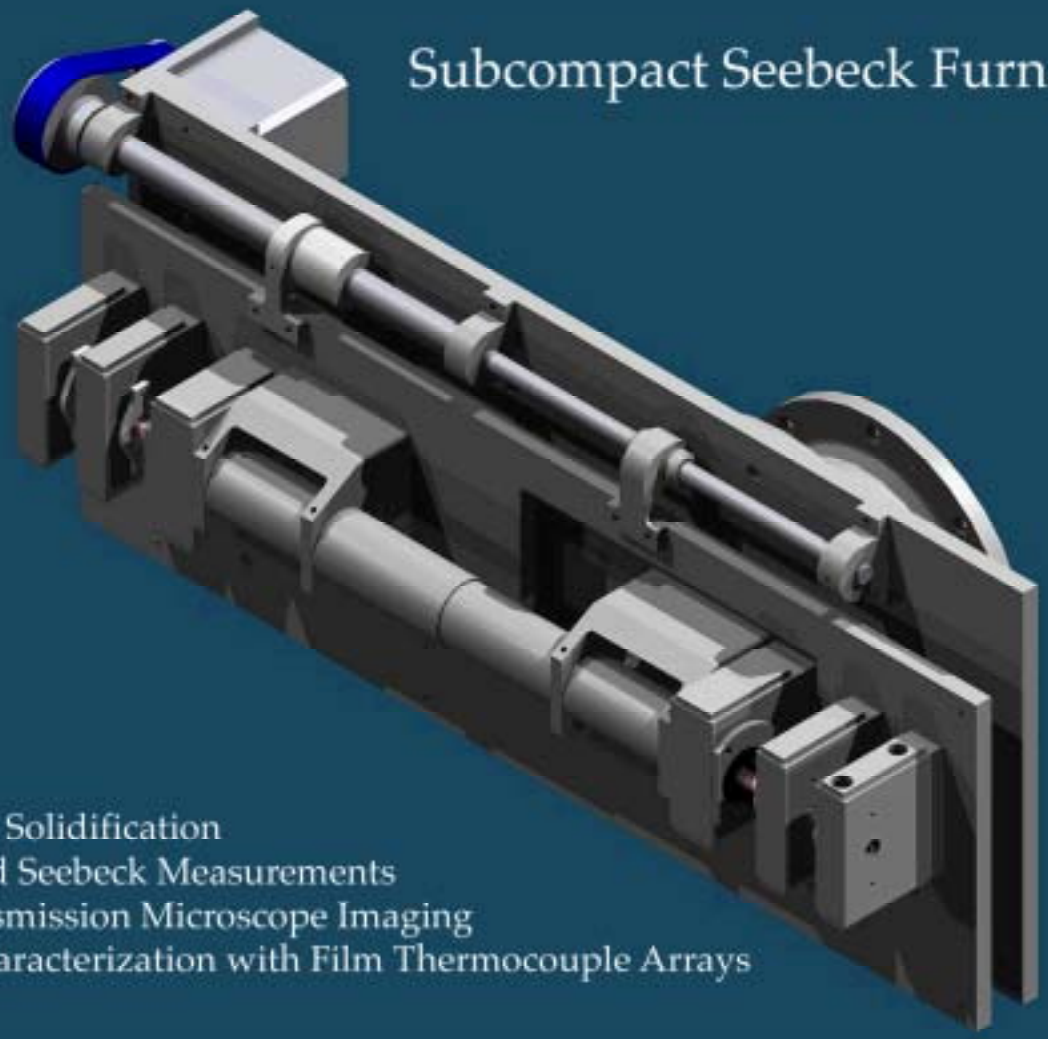


Compact Seebeck Furnace Temperature Profiles During Translation of Left Half



Third-generation “Subcompact Seebeck Furnace”, partially assembled without cooling water, electrical lines, bore tube, sample tube, etc. The inset shows the concentric ceramic tubes which telescope with a matching set in the second half of the furnace. Subsequently installed cooling and other accessories enabled the furnace to be heated to elevated temperatures, approximating the profile needed.

Subcompact Seebeck Furnace Design



- Directional Solidification
- Solid-liquid Seebeck Measurements
- X-ray Transmission Microscope Imaging
- Sample Characterization with Film Thermocouple Arrays

Technology Developments (Continued)

Computer Modeling

- Thermal modeling has assisted in initial furnace designs, confirmed the cause for an excess dip in temperature at the center of the 2nd furnace and assisted in design corrections. A conference presentation was published.
- An Integrated Thermal Modeling of the 3rd- generation furnace is being formulated using a Finite Element Modeling, including radiation.

Hardware and Software for Measurements

- Reference temperatures are controlled to a few hundredths of a degree.
- Voltages are measured with resolutions of 250 nV and less, depending on requirements.

Technology Developments (Continued)

- Furnace scanning, furnace-temperature profiling, sample-temperature profiling, x-ray imaging, solid-liquid Seebeck measurements, conversion of voltages to temperatures and time-stamping and recording techniques for all data have been developed, primarily in Labview®, for user friendliness.

Acknowledgements

Lloyd Love & Nelson Martinez, MSFC, for engineering and design support. Leroy Mullaley, MEVTEC, Curtis Bahr, Don Lovell, Jeff Quick and Penny Pettigrew, Morgan Research, and David Foster and Joe Glover, ERC, for machining, technician, & other assistance. Amber Dickens & Christy Bridges, UAH, for student help.

Nanophase and Composite Optical Materials

Dr. David D. Smith / SD46

Biological and Physical Sciences for Exploration Team

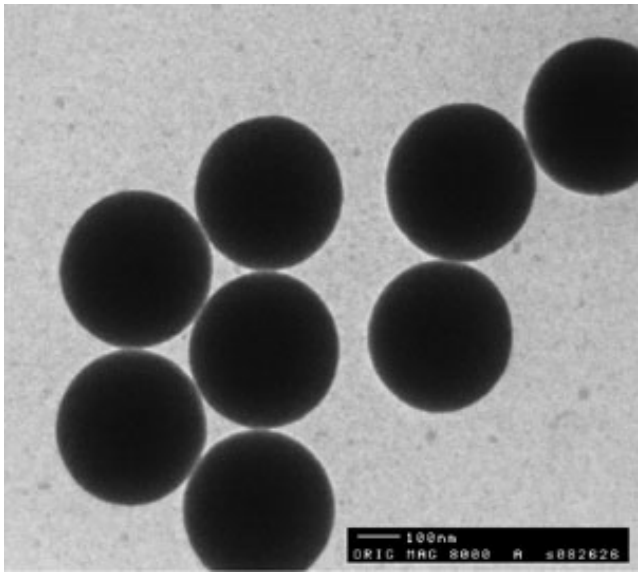
Biological and Physical Space Exploration Laboratory

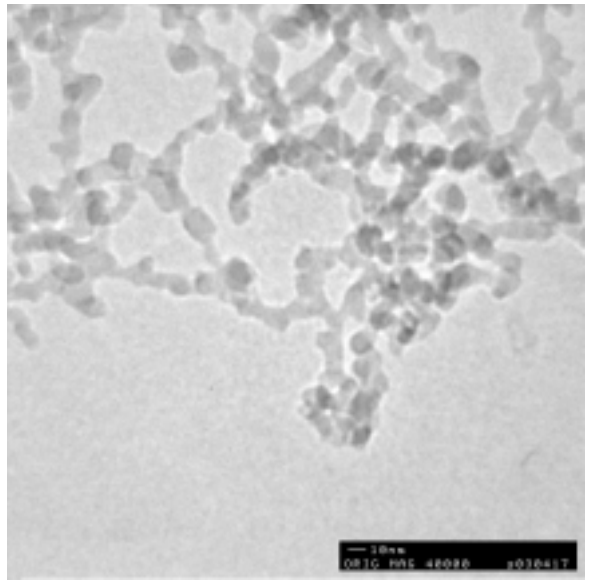
Microgravity Sciences and Applications Department

Science Directorate

06/06/02

Silica Stober Nano-Substrates





Ground: 1g **Space: μg**

- **Gels were formed instead of particles!** ***Conclusion: Microgravity favors the formation of more rarefied structures.***

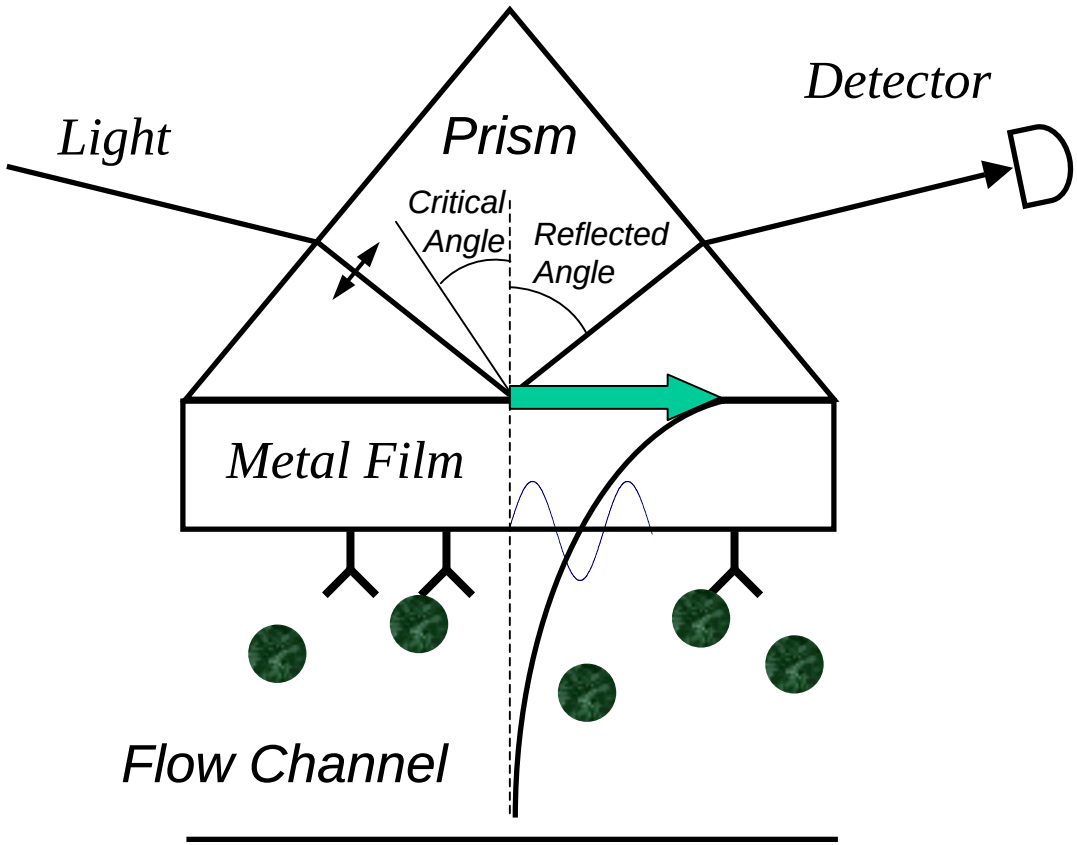
D.D. Smith, L. Sibille, R. Cronise, A.J. Hunt, S.J. Oldenburg, D. Wolfe and N.J. Halas, Langmuir, 2000.

L. Sibille, **D.D. Smith,** in *Polymer Research in Microgravity,* American Chemical Society 2001.

Surface Plasmon Resonance Investigation of Macromolecular Interactions

Applications:

- **Virus Inhibitors**
- **Protein aggregation**
- **Polymer kinetics**
- **Biosensors**

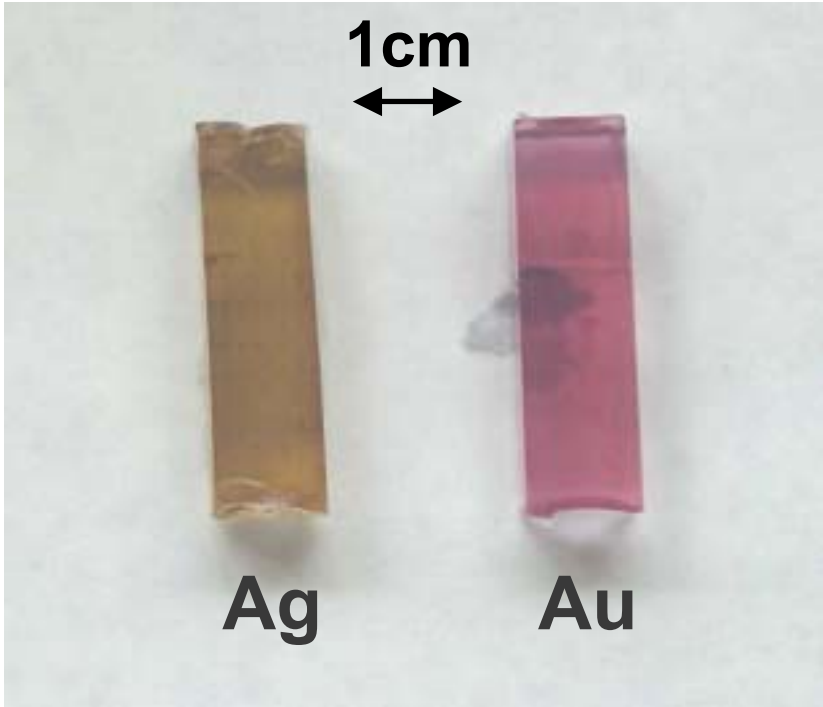


Investigators: **D.D.Smith** (SD46), K. Fuller (UAH), J. Gavira (UAH), J. Ayling (USA)

Colloidal Metal Sol-Gels

Applications:

- **Biofilters**
- **Biosensors**
- **Catalysis**
- **Tunable Nonlinear Optics**

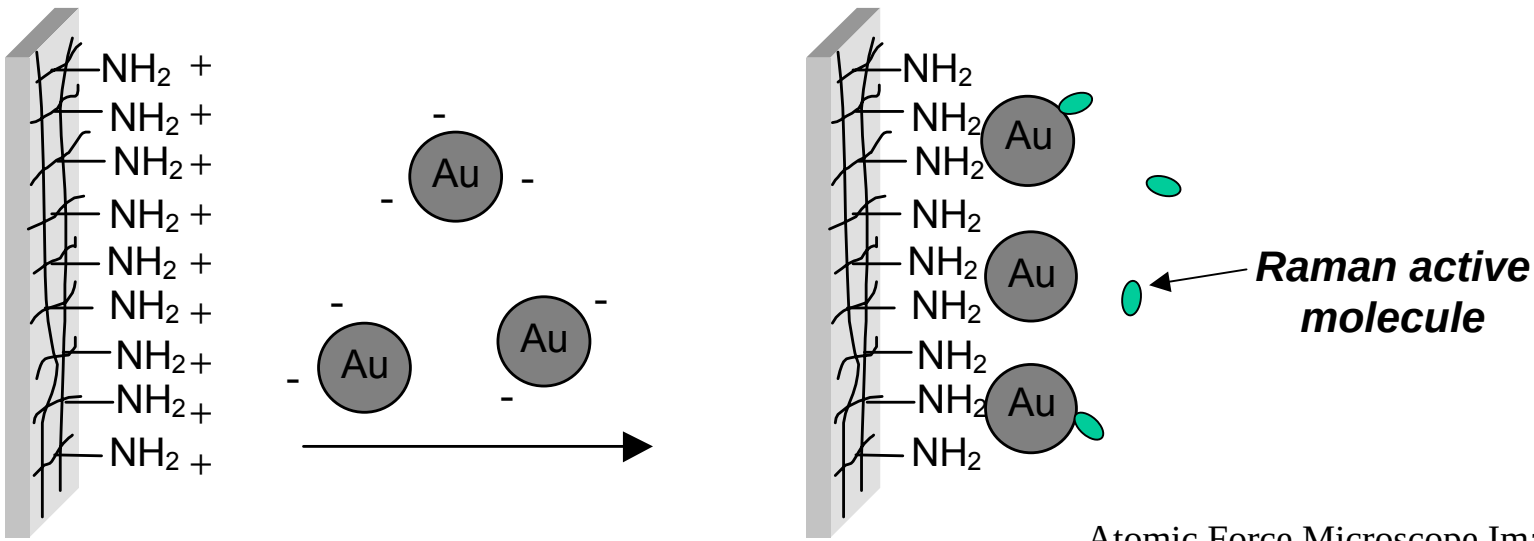


D. D. Smith, L. Sibille, E. Ignont, R. Cronise, D. A. Noever, *J. Non-Cryst. Sol.* **225**, 330, 1998.

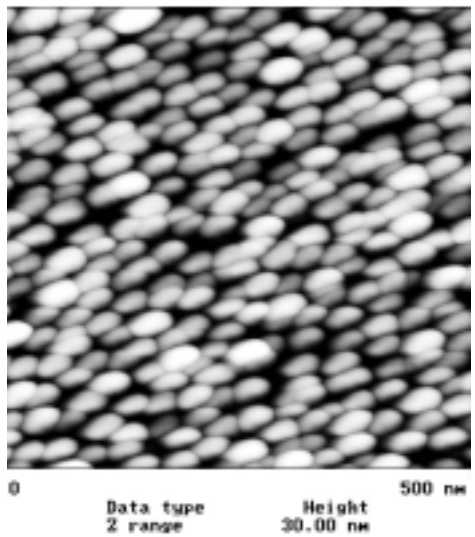
D. D. Smith, L. Sibille, R. Cronise, D. A. Noever, *J. Porous Mat.* **7**, 499, 2000.

D. D. Smith, L. Snow, E. Ignont, L. Sibille, *J. Non-Cryst. Sol.*, **285**, 256, 2001.

Metal Nanoparticle Substrates



Atomic Force Microscope Image

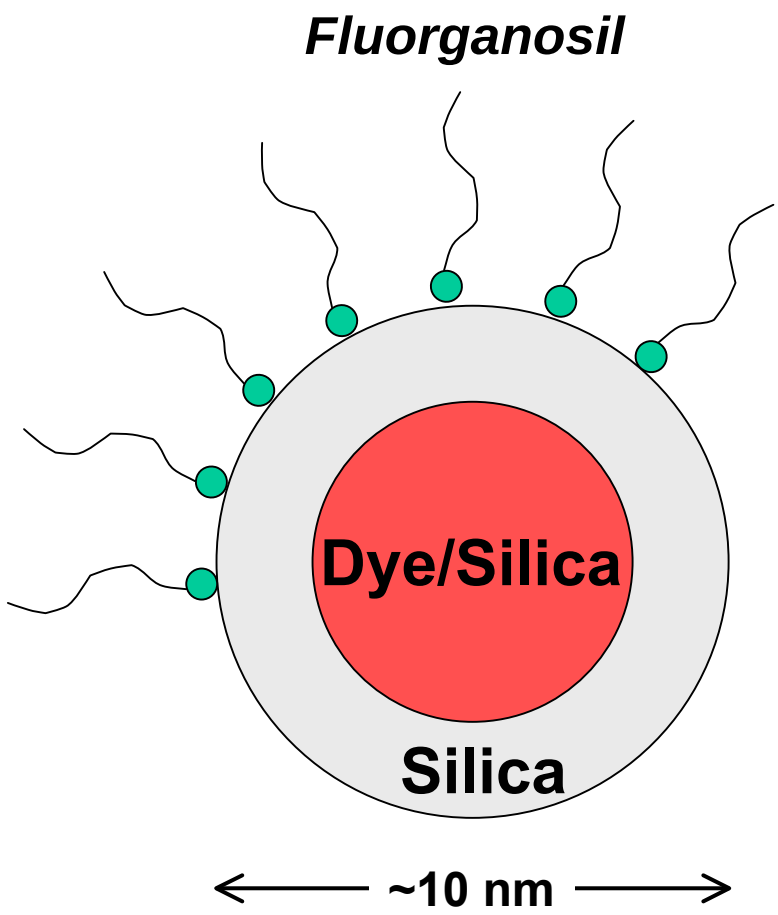


- **Rationale:**
  - **Self-assembled alkane-silane monolayers used to produce colloidal metal monolayers.**
  - **Use of metal nanoparticles enables control over surface roughness.**
  - **Enormous enhancement in local electric field near a metal nanoparticle.**
- **Applications:**
  - **Surface Enhanced Raman Scattering**
  - **Enhanced Fluorescence**
  - **Nanoparticle Enhanced Power (Nano-PEP): Potential for increased solar cell efficiency.**

B. Wendling, Ph.D. Thesis

Fluorescent Silica Nano-Sols

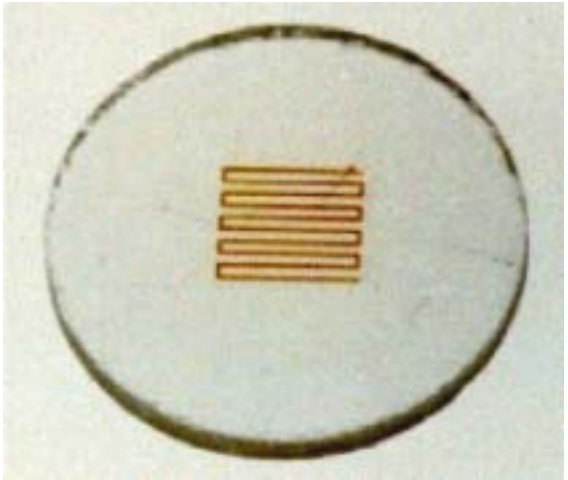
- Accomplishments:
  - Developed fluorescent organophilic silica nanosols (fluoroganosils).
  - Used the particles to evaluate theories of spontaneous emission in dielectric media. Ruled out one theory.
- Applications of fluorganosils:
  - Water detoxification and monitoring
  - Environmental and medical tracers
  - Biosensors
  - Paints (reversible and stealth)
  - Immunoassays
  - Chromatography
  - Electrically insulating films
  - Anti-stick/Anti-static films
  - Delustering (anti-sheen) agents



Investigators: D.D.Smith (SD46), W. Patterson (UAH)

Photodeposition of Polymeric Thin Films

Masked Substrate



Direct Write Lithography

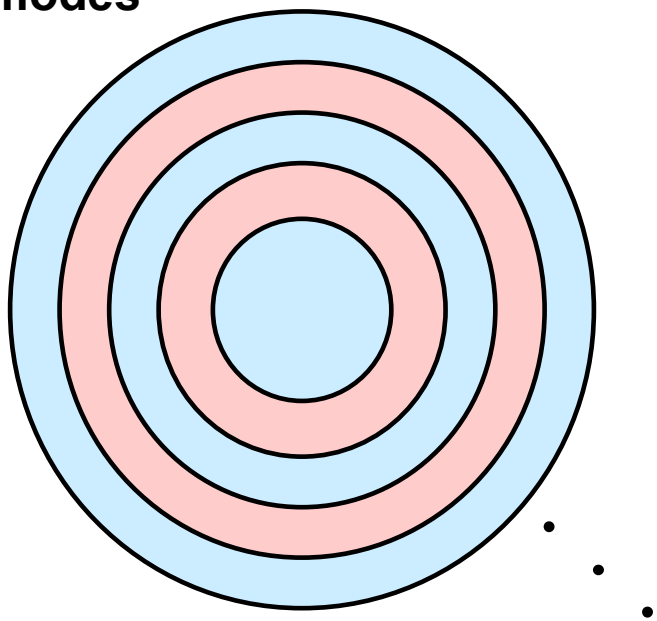
Composite Nonlinear Optic Fiber

- **Photodeposition of nonlinear optical polydiacetylene thin films occurs directly form solution via ultraviolet irradiation, enabling improved processing of waveguides and other structures.**

Investigators: M.S.Paley (USRA), D.D.Smith (SD46), H.Chang (UAH), W.K.Witherow (SD46), D.O.Frazier (SD01)

Spherical Photonic Band-Gap Materials

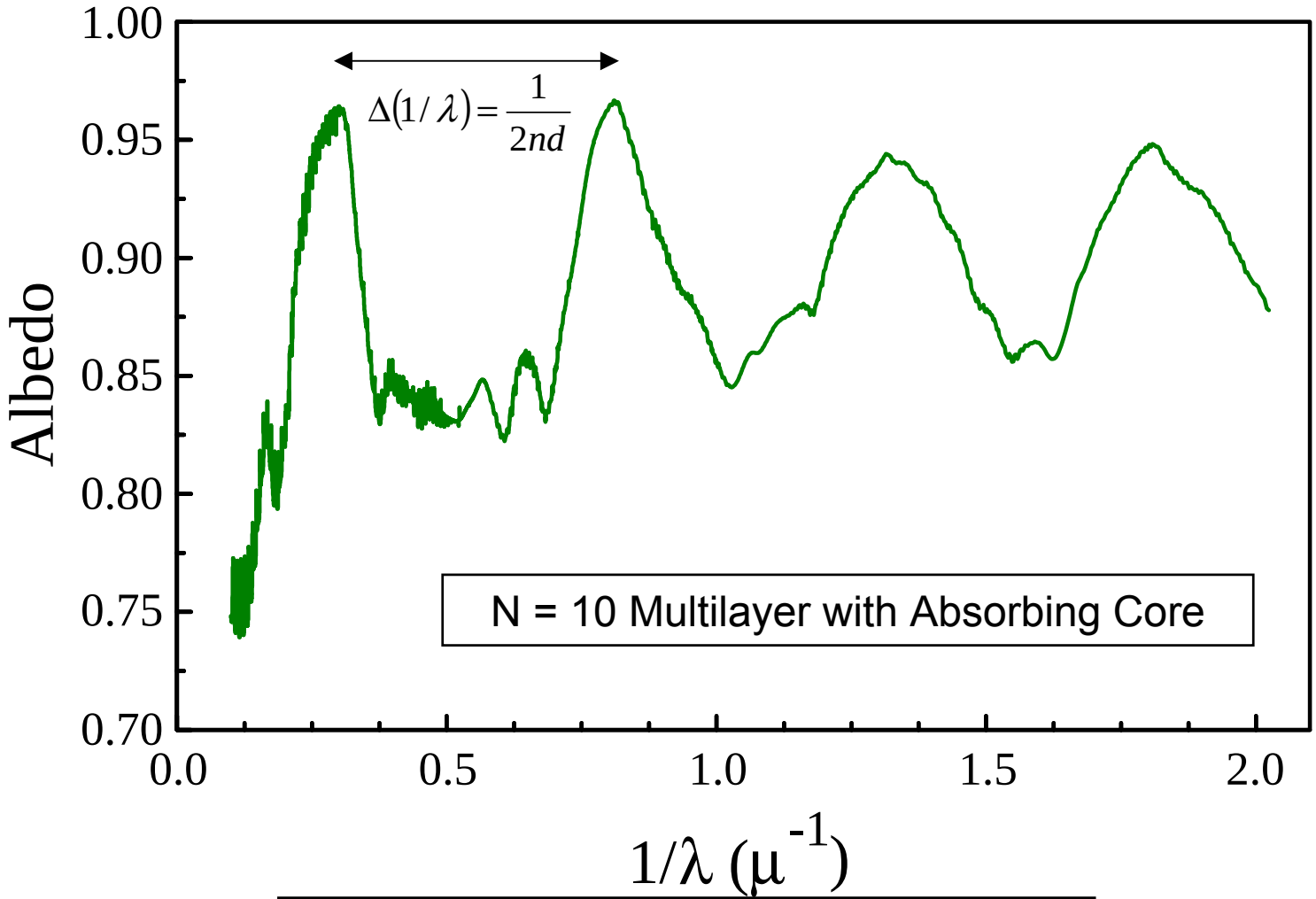
- **Predicted novel behaviors in concentric multilayers:**
  - **Quarter wave bands in the scattering**
  - **Mode splitting of whispering gallery modes**
- **Potential Applications:**
  - **Atmospheric Engineering**
  - **Fusion**
  - **Vehicle health monitoring**
  - **Biosensors**
  - **Slow light**
  - **Optical Communications**



D.D.Smith, K. Fuller, *J. Opt. Soc. Am. B*, 2002.

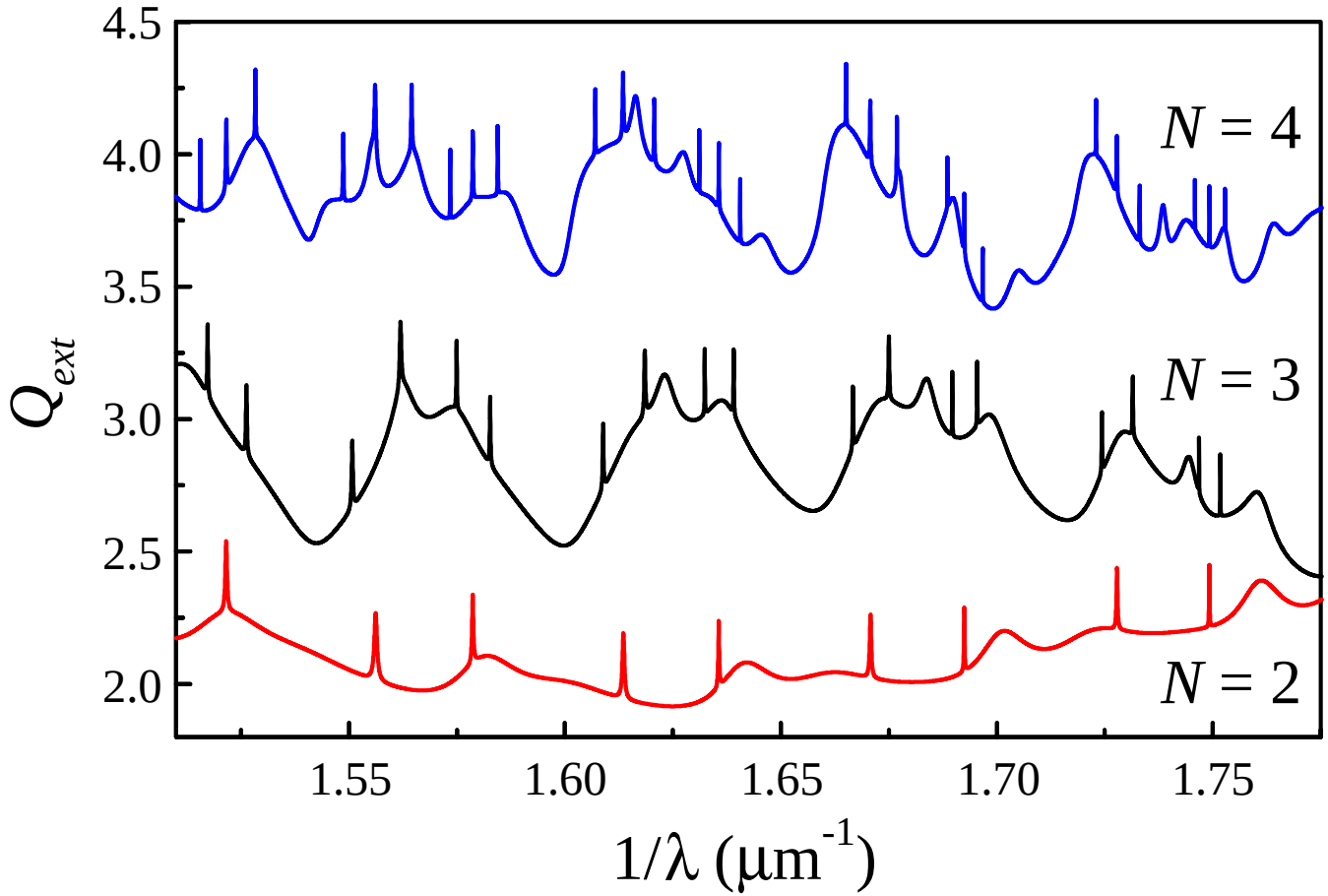
D.D.Smith, H.Change, K.Fuller, *J. Opt. Soc. Am. B*, 2002.

Photonic Bands in Albedo



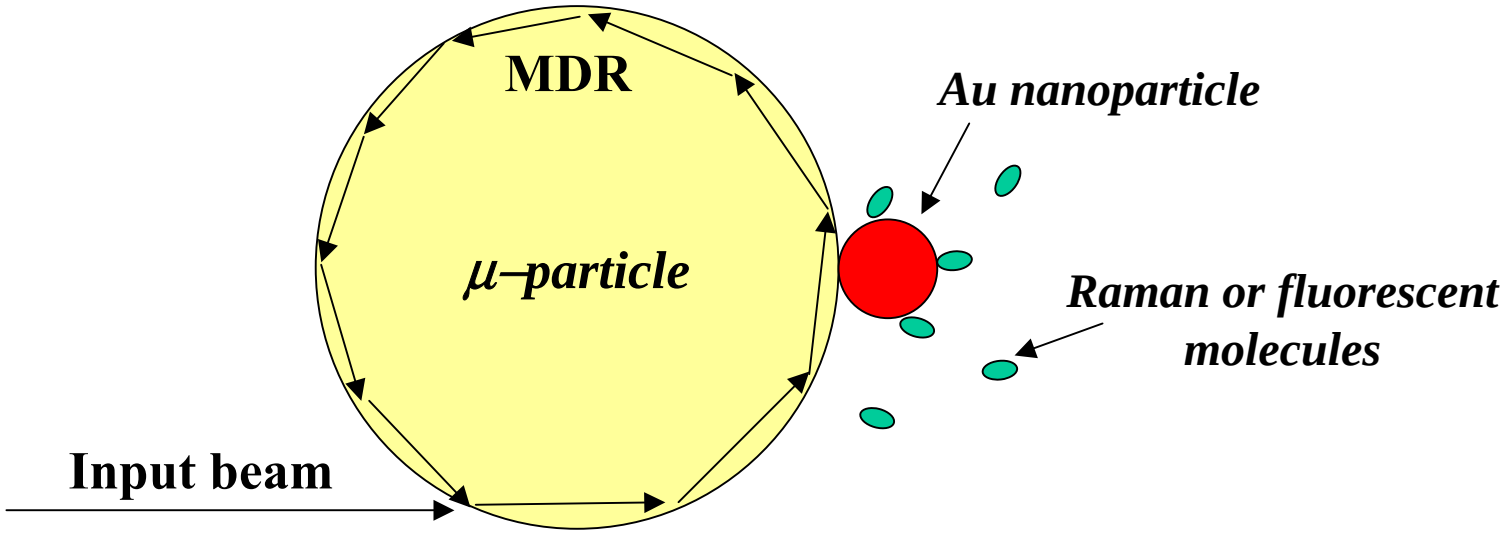
D.D. Smith, K. Fuller, *Special Issue of JOSA B*, 2002.

Whispering Gallery Mode Splitting



D.D. Smith, H. Chang, K. Fuller, JOSA B, 2002.

Cavity Assisted Spectroscopic Analysis (CASA)



- **Au particle acts as antenna and funnels light into and out of the m-particle**
- **Au absorption improved by several orders of magnitude.**
- **Resulting higher local fields lead to improved SERS (CASERS), Fluorescence detection (CAF)**

Funded By: Education Programs Office; Collaborators: K. Fuller (UAH SFFP), A. Gates (UAH)

Silicon Detector System for Cross Section Measurements

Dr. James H. Adams, Jr.

In order to estimate the radiation shielding effectiveness of materials it is necessary to know cosmic ray particles are broken up as they pass though these materials. The breakup of cosmic ray particles is characterized the nuclear fragmentation cross sections, i.e. an effective geometrical cross section assigned to each target nucleus that represents its apparent size for fragmenting the incident particle. The values of these cross sections depend on the details of nuclear physics and cannot be calculated from first principles owing to the many-body nature of the interactions. The only way to determine them is to measure them. Once a sufficient number of cross sections have been measured, the systematic nature of the interactions allows other cross-sections to be estimated. The number of cross sections that contribute to the estimation of shielding effectiveness is very large ~10,000. Fortunately most make minor contributions. These can be estimated from nuclear systematics. Only those who's uncertainties make significant contributions to the error in the shielding effectiveness estimations need to be measured.

In the past it has proven difficult to measure light fragment production cross sections from the interactions of heavy cosmic rays owing to the size of the detectors used. We have developed a highly pixilated silicon detector system that can individually identify these light fragments while making efficient use of costly accelerator time. This system is an outgrowth of detector technology developed under a CDDF and a Code S sponsored cosmic ray experiment.

THE ZERO-DEGREE DETECTOR SYSTEM

James H. Adams, Jr.

Marshall Space Flight Center

and

Evgueni Kouznetsov

University of Alabama in Huntsville

The purpose of this investigation is to develop a means of measuring the production cross sections for light fragments from heavy ion collisions with shielding material target nuclei.

The approach is to construct a large number of small charged particle telescopes using 1 cm^2 silicon detectors.

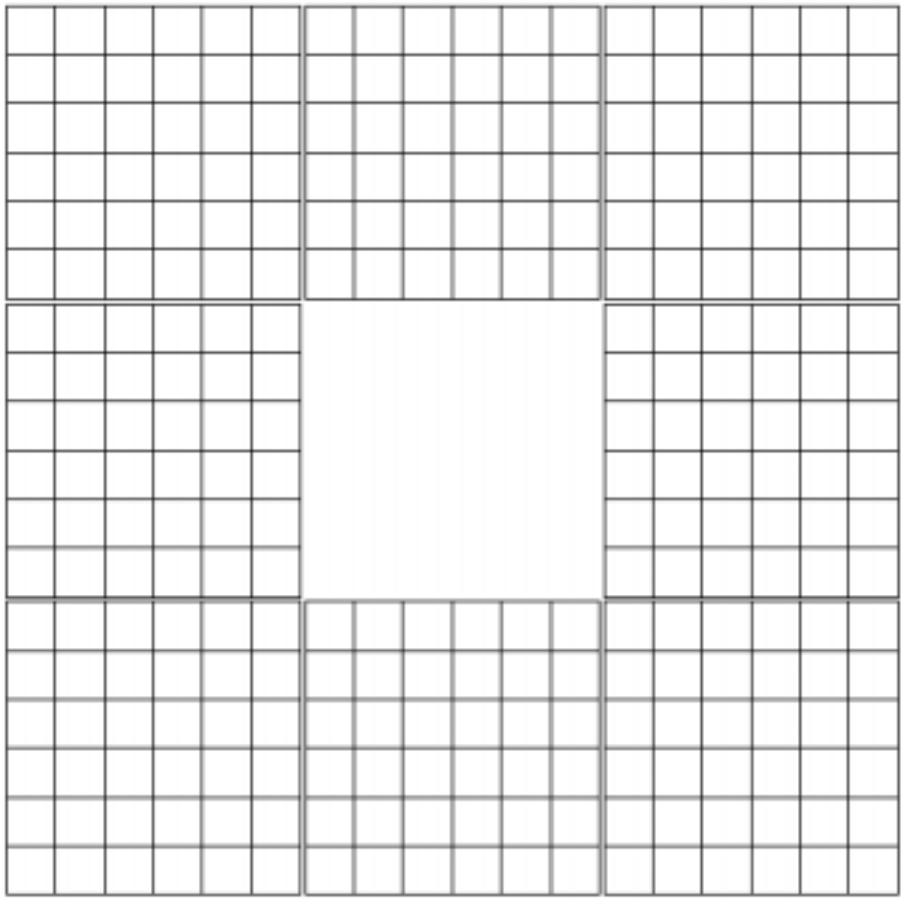


Figure 1. Construction of one layer of silicon detectors in the ring

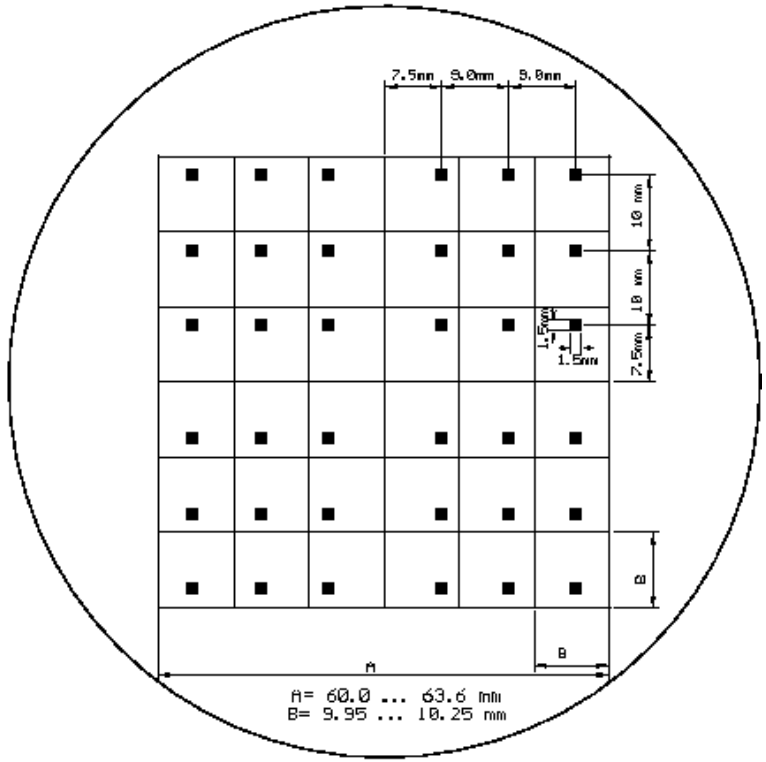


Figure 2. 36-pad detector unit with windows for bonding made from 4-inch wafer

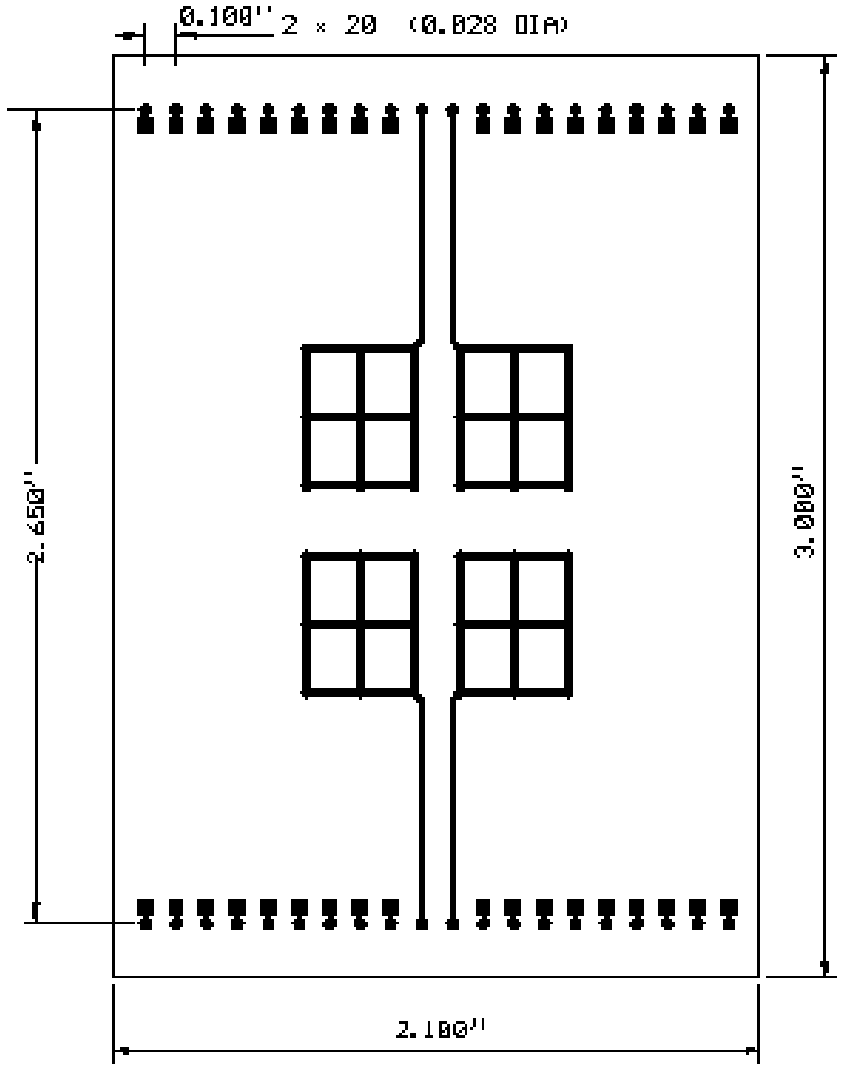


Figure 3. Ceramic substrate

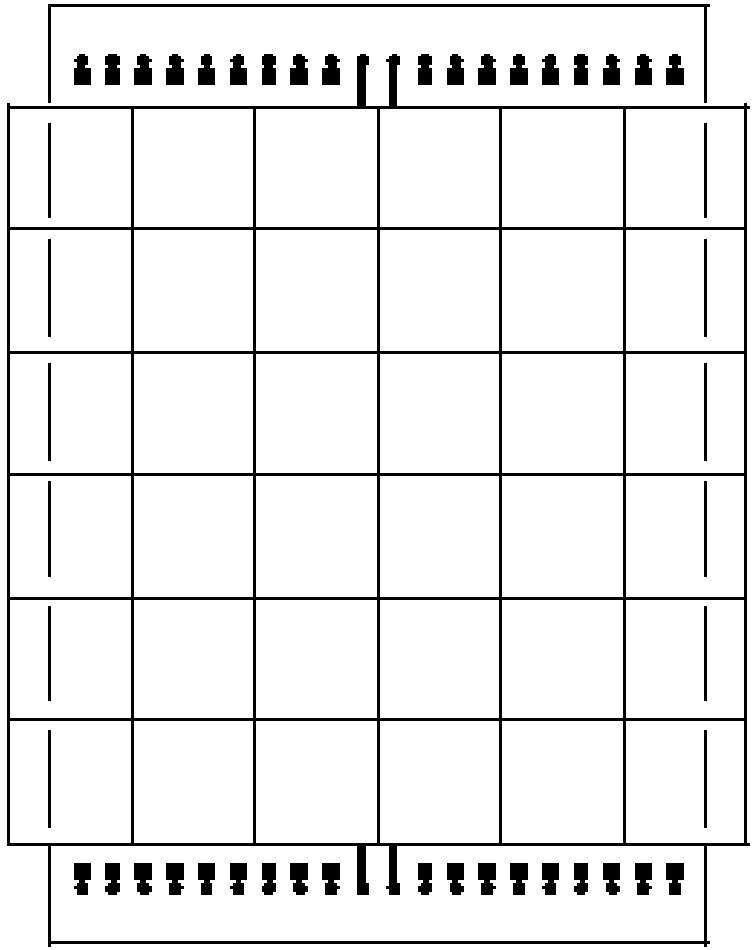


Figure 4. Silicon detector mounted on a ceramic substrate to form a detector card

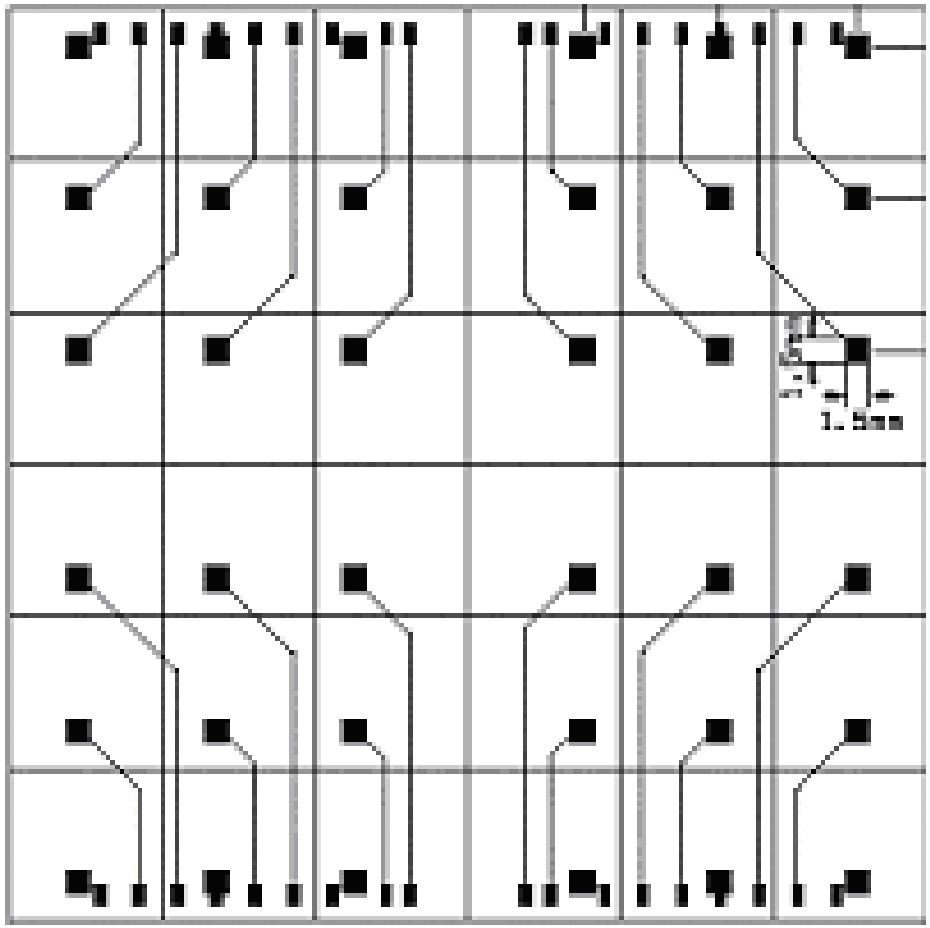


Figure 5. Aluminum traces deposited upon the passivation and routed signals from detector pads to two opposite detector edges

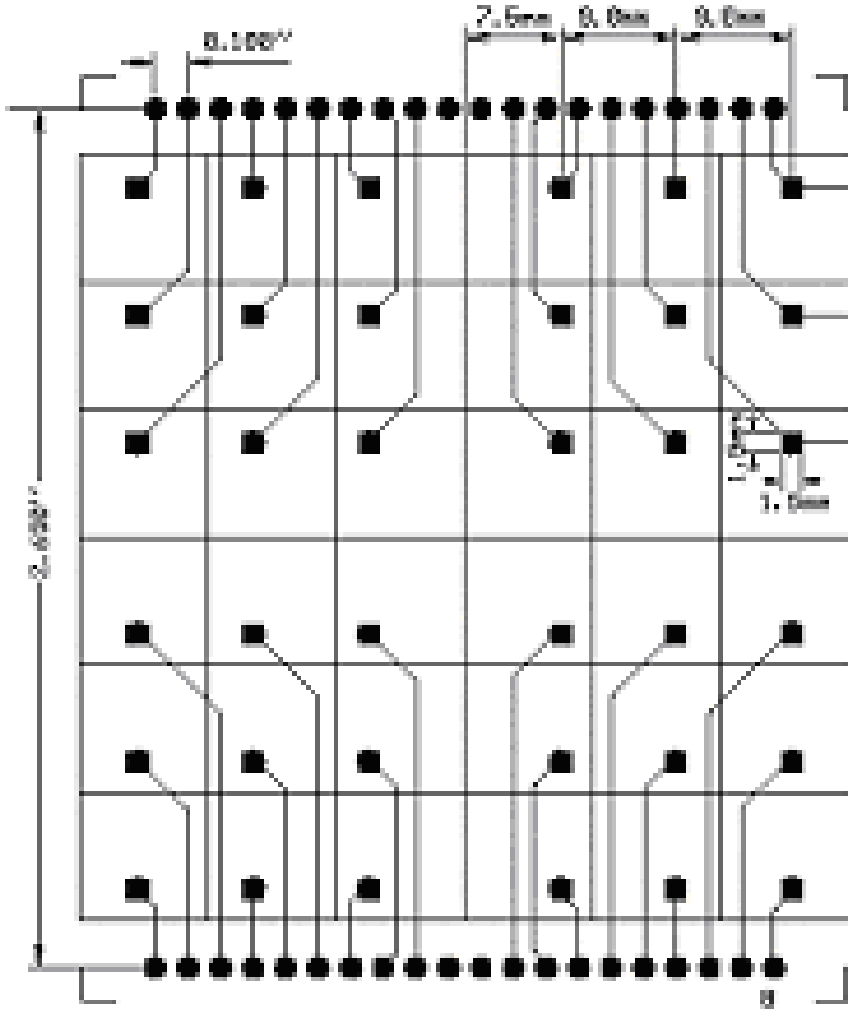


Figure 6. Flexible kapton foil with traces attached above the detector for routing signals from detector pads to two rows of pins.

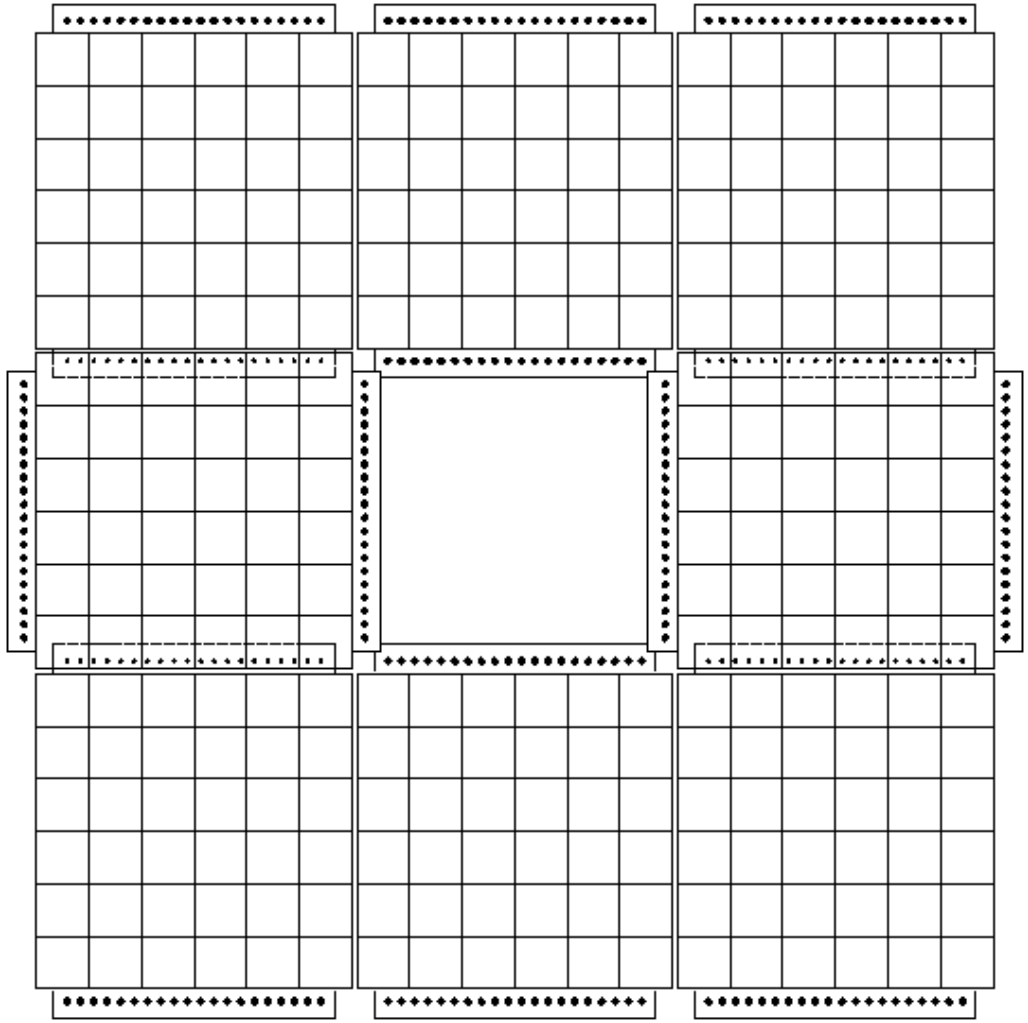


Figure 7. Orientation of the ceramic Detector Cards on the Motherboard

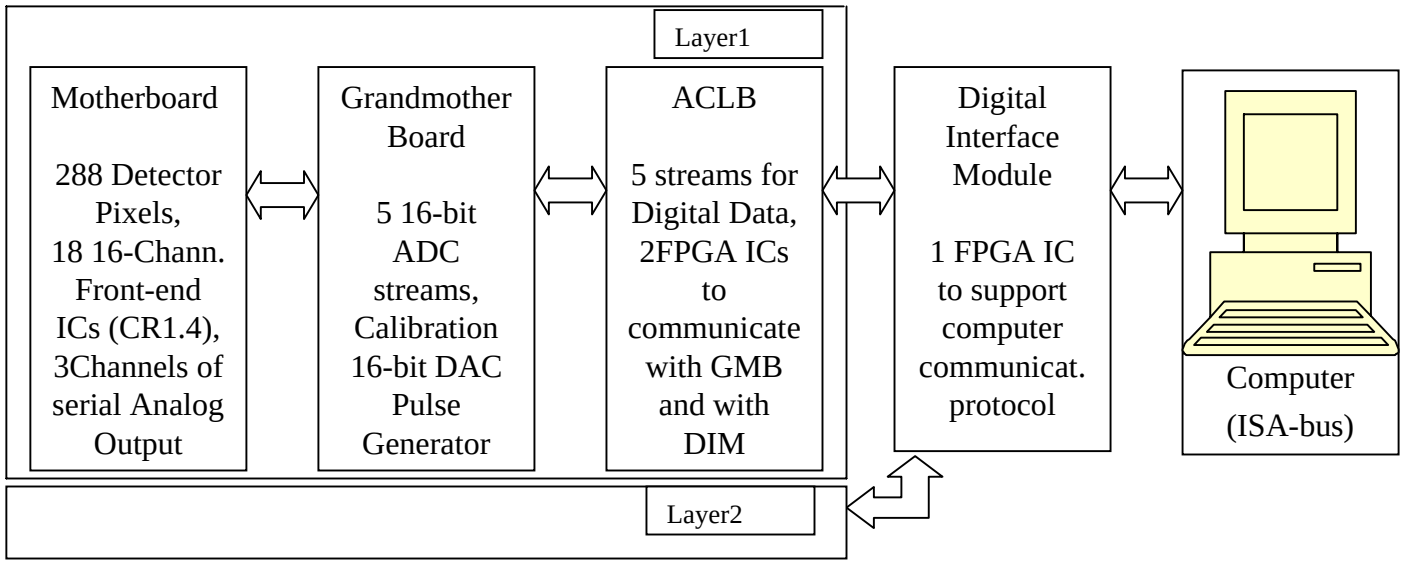


Figure 8. Functional diagram of Zero-Degree Detector readout .

Conclusions

We have developed a detector that:

1) Has small pixels to separately measure light fragments

2) Makes efficient use of beam time

This enables the complete measurement of heavy ion nuclear fragmentation cross sections for the first time.

Appendix B

Materials Science Team

Title	Presenter	Page
"Materials Science Overview"	Dr. Frank Szofran, Dr. Donald Gillies	M-1
"Reduction of Defects in Germanium-Silicon (RDGS)"	Dr. Frank Szofran	M-9
"Effects of Traveling Magnetic Field on Dynamics of Solidification"	Dr. Konstantin Mazuruk	M-26
"Uses of Computed Tomography for Characterizing Materials Grown Terrestrially and in Microgravity"	Dr. Donald Gillies	M-44
"An Overview of the Materials Science Research at the MSFC Electrostatic Levitator Facility and Recent CDDF Efforts"	Dr. Jan Rogers	M-62
"The Role of Convection and Growth Competition on Phase Selection in Microgravity (LODESTARS)"	Dr. Robert Hyers	M-81
"Studies of Nucleation and Growth, Specific Heat and Viscosity of Undercooled Melts of Quasicrystals and Polytetrehedral-Phase-Forming Alloys (QUASI)"	Dr. Robert Hyers	M-94
"Succinonitrile Purification Facility"	Louise Strutzenberg	M-104
"Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport"	Dr. Ching-Hua Su	M-108

Materials Science Team

Title	Presenter	Page
"Structural Fluctuation and Thermophysical Properties of Molten II-VI Compounds"	Dr. Ching-Hua Su	M-126
"Laboratory and In-Flight In-Situ X-ray Imaging and Scattering Facility for Materials, Biotechnology and Life Sciences"	Dr. Ching-Hua Su	M-142
"Evolution of Local Microstructures: Spatial Instabilities in Coarsening Clusters"	Dr. Donald Frazier	M-146
"Spaceflight Holography Investigation in a Virtual Apparatus (SHIVA)"	William Witherow	M-159
"Particle Engulfment and Pushing By Solidifying Interfaces (PEP)"	Dr. Subhayu Sen	M-173
"Numerical modeling and fluids experiments for materials processing and protein crystallization."	Dr. Narayanan Ramachandran	M-184

Materials Science Overview

Dr. Donald C. Gillies/SD41

Discipline Scientist

Dr. Frank R. Szofran/SD46

Team Lead

Materials Science Program Structure

NASA HQ

- responsible for program content and selection
- Enterprise Scientist (Wargo)

NASA MSFC

- responsible for implementation of ground and flight programs
- Discipline Scientist (Gillies) and Discipline Manager (Schlagheck)

Advisory Body

- Discipline Working Group (DWG) composed of eminent materials scientists from outside NASA (exceptions are NASA ex officio)
- DWG writes Discipline Document from which NRA content is derived

Evaluation Bodies

- Every three years or so, program is reviewed by (such as)

  Committee on Microgravity Research (current), National Materials Advisory Board, OBPR Maximization and Prioritization (ReMaP) Task Force

Flight Program

Has had as many as 26 PIs in flight and flight definition stage.

Future number will be determined by results of ReMaP Task Force and POP anticipated later this summer.

Each flight project has a NASA-appointed Project Scientist (1/2 time job)

- **assist the PI in understanding and preparing for reviews such as Science Concept Review, Requirements Definition Review and other internal reviews**
- **ensure the PI gets maximum science support from MSFC**
- **fully understand the science and be able to represent the PI's needs to the MSFC community**
- **collaborate with the Project manager to ensure the project is well supported and remains vital.**

<u>Principal Flight Equipment</u>

Materials Science Research Rack – 1 and Microgravity Science Glovebox (see back up chart for more details)

Ground-based Program

Ground-based projects fall into one or more of the following categories:

1. **Intellectual Underpinning of Flight Program**
   - **a - theoretical studies, backed up by modeling and computer simulations.**
   - **b - bring to maturity new research, often by young researchers. At times this work may include preliminary short duration low gravity experiments in KC-135 aircraft or drop tube.**
   - **c - enabling characterization of data sets from previous flights.**
   - **d – thermophysical property determinations to aid PIs**
2. **Radiation shielding.**
3. **Preliminary In Situ Resource Utilization (ISRU). - studies for future long duration missions**
4. **Biomaterials. Primarily this consists of materials issues that will support crew health.**
5. **Nanostructured Materials. (fall partly into classification 1b)**
6. **Advanced Materials for Space transportation Purposes (New no PIs yet)**

NSA Technical Monitors are assigned to each PI to maintain contact. Considered to be a 5% man year effort per PI.

Present and anticipated NRAs

Currently the following ground-based PIs are supported:

33 Investigators from the 1996 NRA, and 59 from the 1998 NRA. Each of the 98 PIs has a technical Monitor. The 96 NRAs are about to expire.

NRA 01-OBPR-05 closed November 27, 2001requested solicitations in biomaterials and materials for radiation shielding. Evaluations completed. Announcements probably delayed till after ReMaP Task Force reports.

NRA 01-OBPR-08 is currently open with requests for proposals in materials sconce, due June 3, 2002

and a special focus theme – "Materials Science for Advanced Space Propulsion." due September 3, 2002.

Belief is that NRAs will be annual now, but budget tightening could slow down the initial solicitation.

MSFC Facilities Supporting Materials Science

- Microgravity Development Laboratory/SD43
- Electrostatic Levitator Facility (presentation)
- SCN Purification Facility (presentation)
- Electron Microscope/Microprobe Facility
- Static and Rotating Magnetic Field Facility
- X-Ray Diffraction Facility
- Furnace Development Laboratory

Discipline Working Group Members for Materials Science

Robert Sekerka, Carnegie Mellon University (Chair)

Tim Anderson, University of Florida

Eugene Benton, University of San Francisco

Jonathan Dantzig, University of Illinois

Richard Hopkins, Consultant

Michael Jaffe, Medical Device Concept Laboratory

John Perepezko, Univerity of Wisconsin

John Rabolt, University of Delaware

Rohit Trivedi, Iowa State Univeristy

Michael Wargo, NASA HQ (ex officio)

Donald Gillies NASA/MSFC (Vice-Chair)

POP 2002 Flight PI Trace

PI	ACRONYM	REVIEW HELD or SCHEDULE	FACILITY CARRIER		ON ORBIT SCIENCE COMPLETE	
			BEFORE REPLAN	AFTER REPLAN	BEFORE POP 01 REPLAN	POP 02 REPLAN
91 NRA						
Andrews, Barry	CGH	4 RDR	MSRR-1/QMI	MSRR-1/QMI	FY2008	FY2007
Stefanescu, Doru	PEP	4 RDR	MSRR-1/QMI	MSRR-1/QMI	FY2008	FY2007
Voorhees, Peter	CSLM-2	4 ICR	MSG	MSG	FY2002	FY2003
94 NRA						
Poirier, David	CSS	4 SCR	MSRR-2/EM5	MSRR-1/QMI	FY2010	FY2010
Trivedi, Rohit	IPSIDS	4 SCR	MSRR-2/EM5	MSRR-1/QMI	FY2010	FY2010
96 NRA						
Day, Delbert	CROMIS	4 SCR	MSRR-1/LGF	MSRR-1/LGF	FY2005	FY2009
German, Randall	GEDS	4 SCR	MSRR-1/LGF	MSRR-1/LGF	FY2006	FY2009
Pojman, John	TIPMPS	4 SCR	MSG	MSG	FY2004	FY2009
Szofran, Frank	RDGS	4 SCR	MSRR-1/LGF	MSRR-1/LGF	FY2009	FY2010
Trolinger, James	SHIVA	4 SCR	MSG, ER, FIR	MSG	FY2005	FY2008
98 NRA						
Flemings, Merton	LODESTARS	-3rd Qtr CY02	MSL-EML	MSL-EML	FY2006	FY2006
Kelton, Kenneth	QUASI	-3rd Qtr CY02	MSL-EML	MSL-EML	FY2006	FY2006
Trivedi, Rohit	DSIP	-1st Qtr CY03	DECLIC	DECLIC (No unique chamber)	FY2005	FY2007

Note: MSRR-1 investigations support Core Plus Science

QMI – Quench Module Insert

LGF – Low Gradient Frunace (ESA)

EML – Electromagnetic Levitator (European)

DECLIC – Dispositif pour l'Etude de la Croissance et des Liquides Critiques

ER – EXPRESS Rack

MSG _ Microgravity Science Glovebox

Chart from Ron Schlagheck

Reduction of Defects in Germanium-Silicon (RDGS)

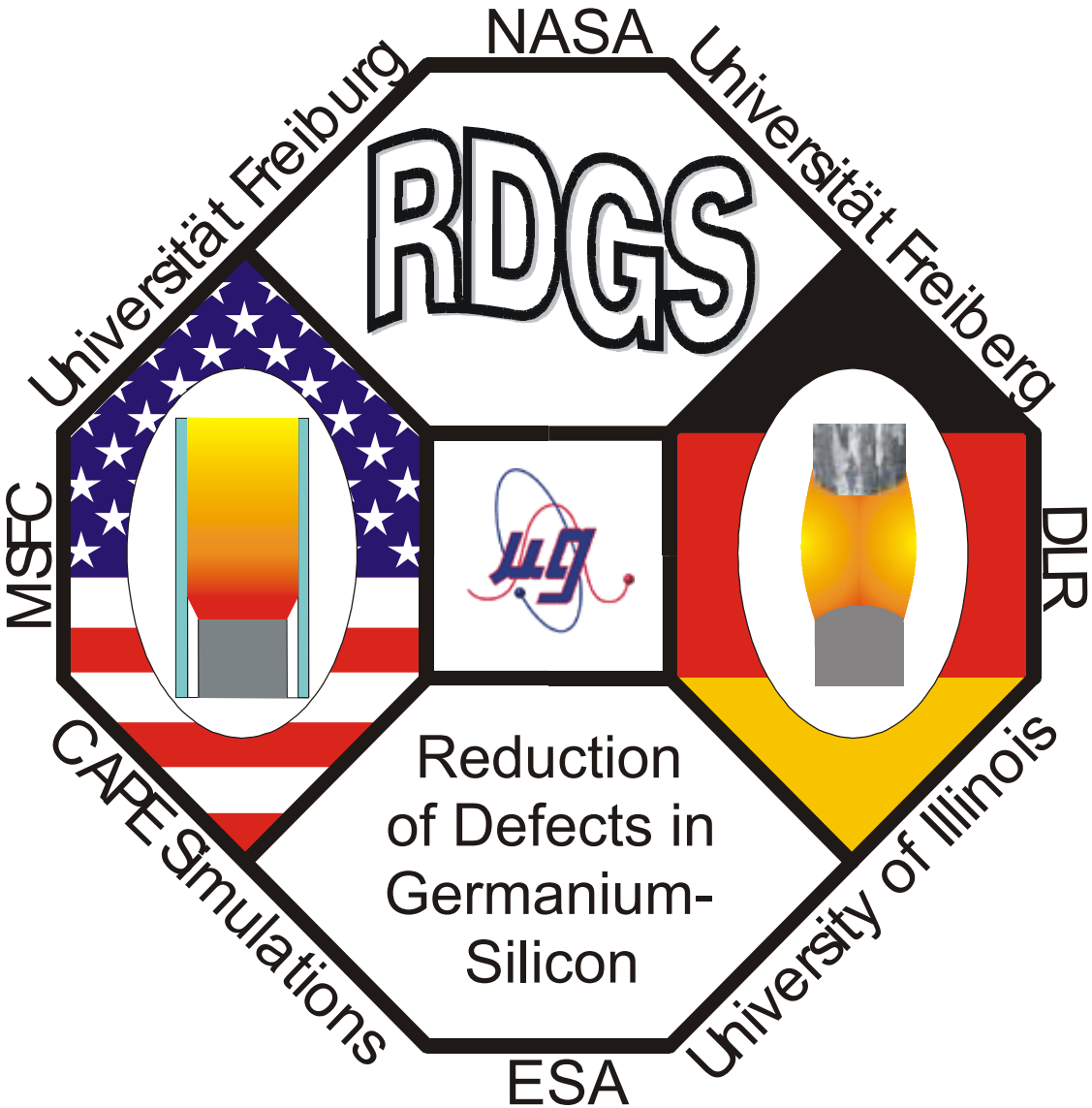
Flight experiment awarded by 96 NRA, SCR completed in December 2000

Principal Investigator: Dr. Frank R. Szofran, NASA/MSFC/SD46

Co-Investigators:

Prof. Dr. K. W. Benz, University of Freiburg, Germany
Dr. Sharon D. Cobb, NASA/MSFC/SD46
Prof. Dr. Arne Cröll, University of Freiberg, Germany
Dr. Peter Dold, University of Freiburg, Germany
Dr. Shariar Motakef, Cape Simulations, Inc.
Dr. Martin P. Volz, NASA/MSFC/SD46
Prof. John S. Walker, University of Illinois at Urbana-Champaign

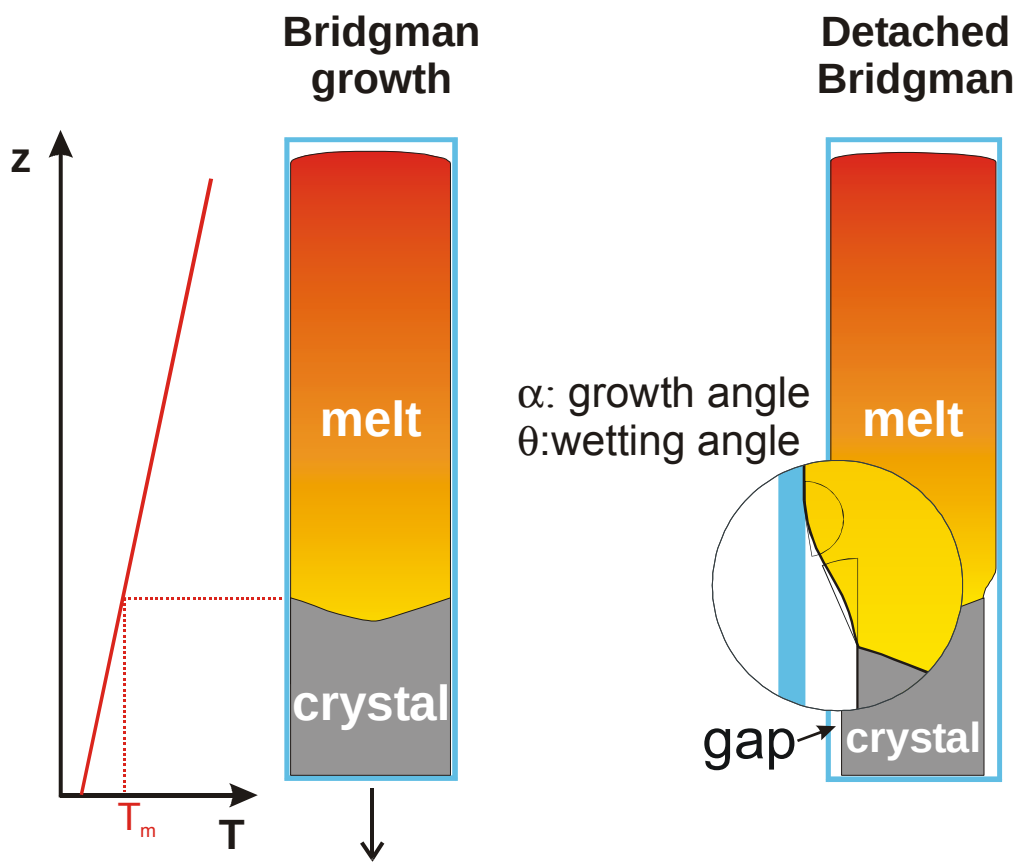
Crystals grown without contact with a container have far superior quality to otherwise similar crystals grown in direct contact with a container. In addition to float-zone processing, detached-Bridgman growth is a promising tool to improve crystal quality, without the limitations of float zoning or the defects introduced by normal Bridgman growth. Goals of this project include the development of the detached Bridgman process to be reproducible and well understood and to quantitatively compare the defect and impurity levels in crystals grown by these three methods. Germanium and germanium-silicon alloys are being used. At MSFC, we are responsible for the detached Bridgman experiments intended to differentiate among proposed mechanisms of detachment, and to confirm or refine our understanding of detachment. Because the contact angle is critical to determining the conditions for detachment, the sessile drop method was used to measure the contact angles as a function of temperature and composition for a large number of substrates made of potential ampoule materials. Growth experiments have used pyrolytic boron nitride (pBN) and fused silica ampoules with the majority of the detached results occurring predictably in the pBN. Etch pit density (EPD) measurements of normal and detached Bridgman-grown Ge samples show a two order of magnitude improvement in the detached-grown samples. The nature and extent of detachment is determined by using profilometry in conjunction with optical and electron microscopy. The stability of detachment has been analyzed, and an empirical model for the conditions necessary to achieve sufficient stability to maintain detached growth for extended periods has been developed. We have investigated the effects on detachment of ampoule material, pressure difference above and below the melt, and silicon concentration; samples that are nearly completely detached can be grown repeatedly in pBN. Current work is concentrated on developing a method to make in situ pressure measurements in the growth ampoules.


NASA
Universität Freiberg
Universität Freiburg
RDGS
MSFC
DLR
CAPE Simulations
University of Illinois
Reduction
of Defects in
Germanium-
Silicon
ESA

Detached Bridgman Growth: Principles

Sufficient condition for detachment[1,2]:

$$(\alpha + \theta \geq 180°)$$



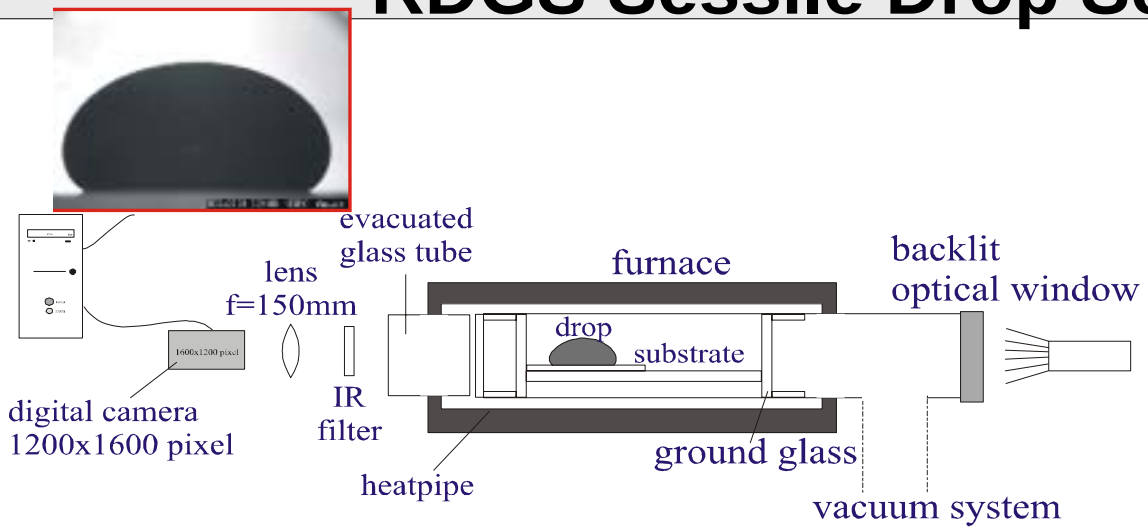
Advantages

- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

[1] V. S. Zemskov: Fiz. Khim. Obrab. Mater. 17 (1983) 56

[2] T.Duffar, I.Paret-Harter, P.Dusserre: J.Crystal Growth 100 (1990) 171.

RDGS Sessile Drop Setup



T_{max}: 1100°C

Dynamic vacuum
Argon
Forming Gas

Opt. resolution: 25µm
(diffraction limited)

Detached Growth with Forced Pressure Difference

T-Profile a)
(p_1=p_2)

↓

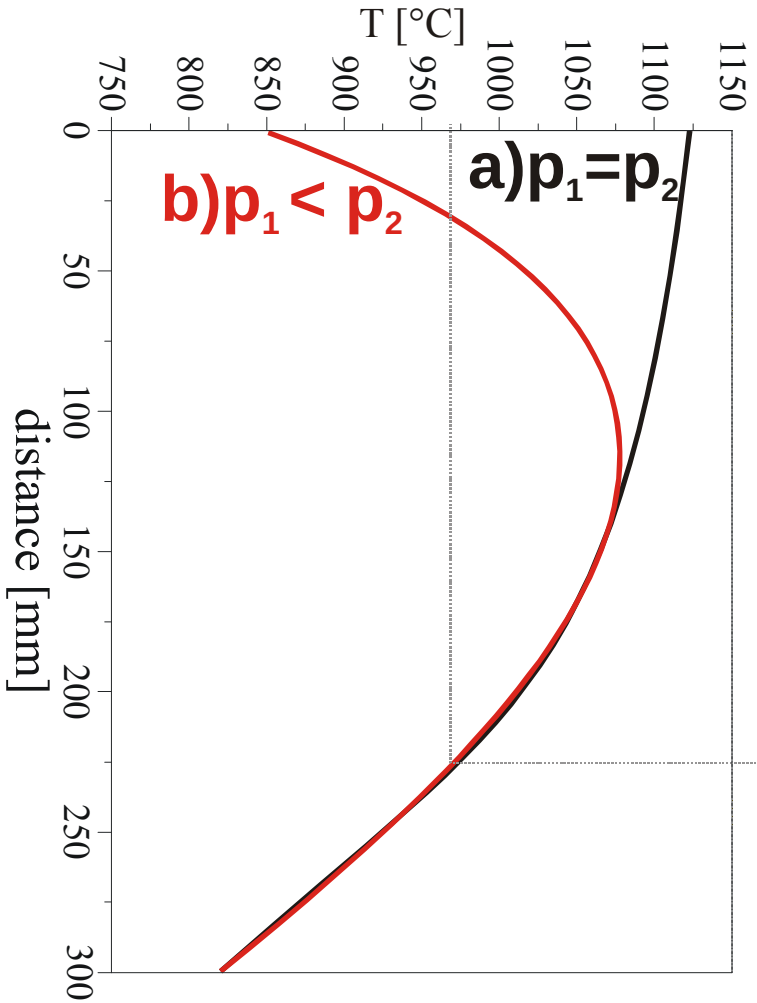
Melting of feed material
(p_1=p_2)

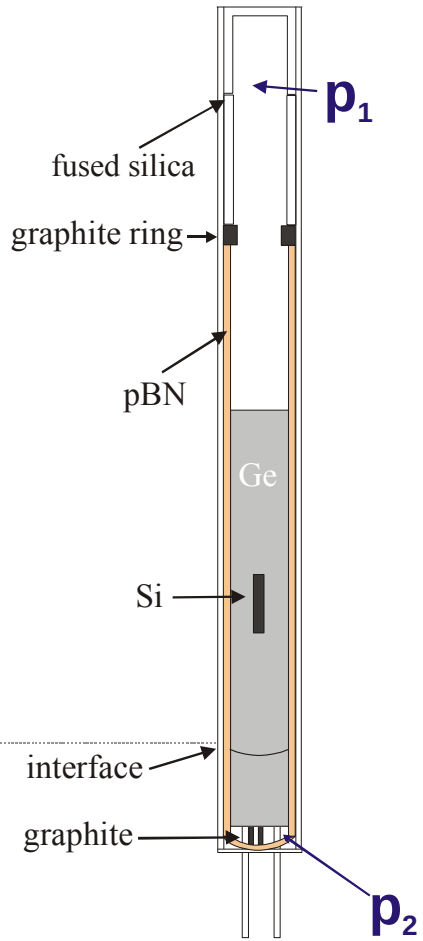
↓

T-Profile b)
(p_1<p_2)

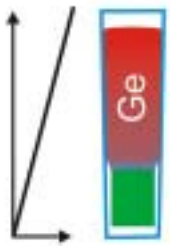
↓

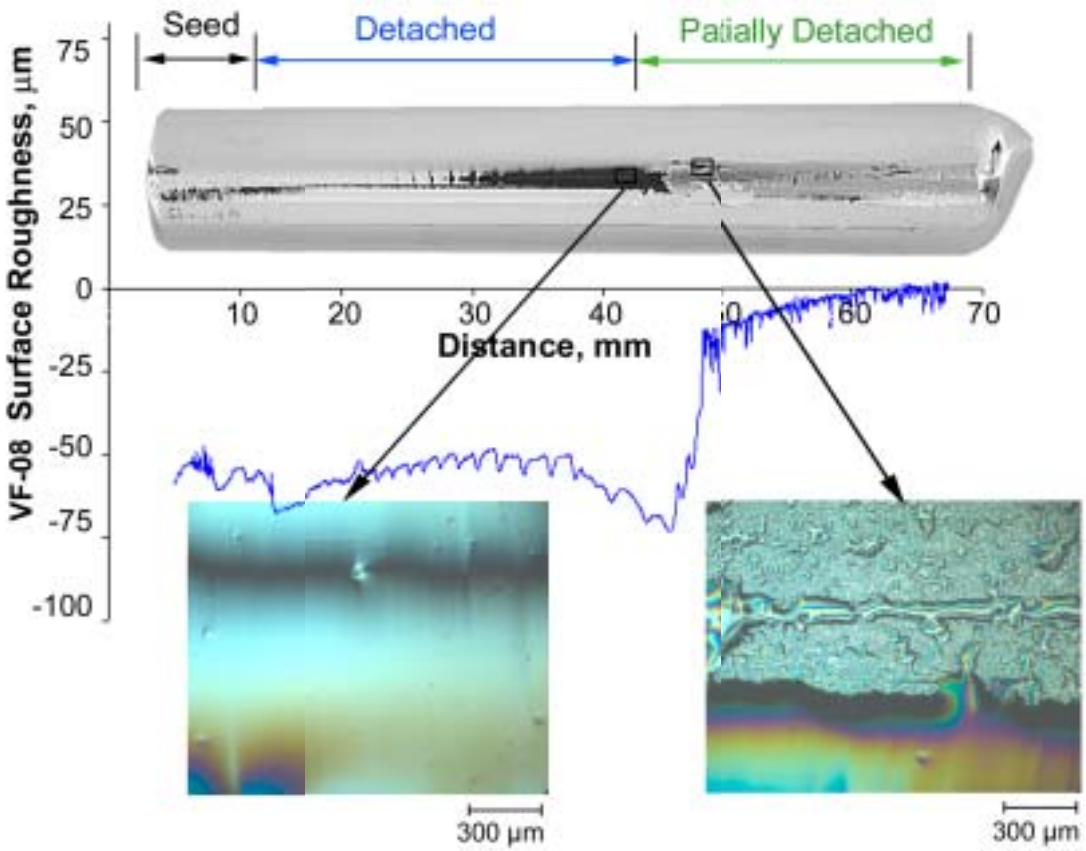
Translation
(p_1<p_2)





Effect of Closed Bottom pBN Ampoule





➢ **For Ge in a closed pBN ampoule, enough pressure develops in the gap to produce detachment.**

Detached vs Attached Etch Pit Densities

Completely detached grown crystal UMC7

1mm

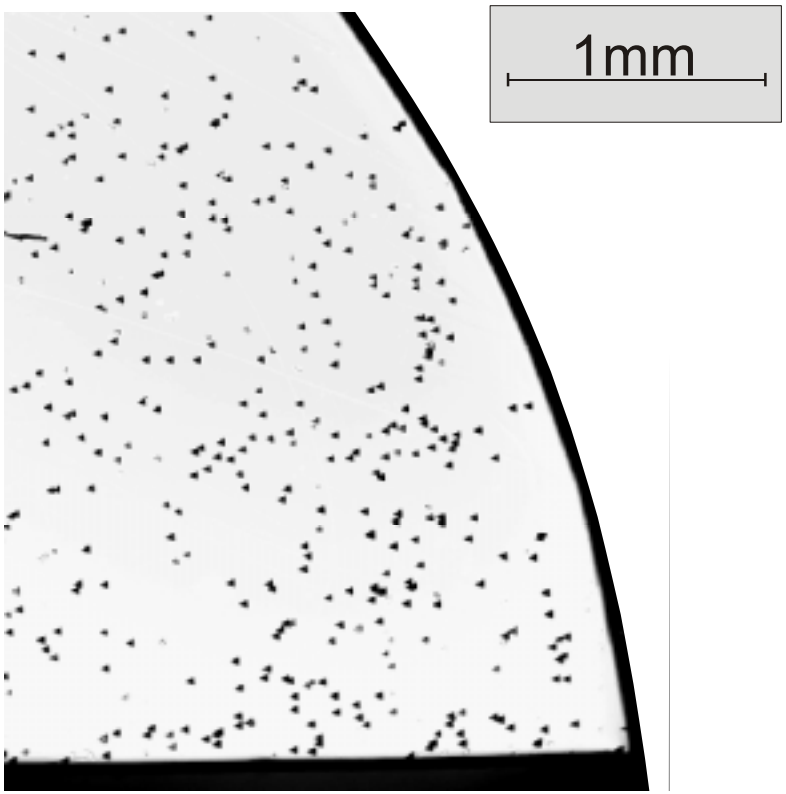
Attached grown crystal UMC6

EPD ≈ 200cm^{-2}

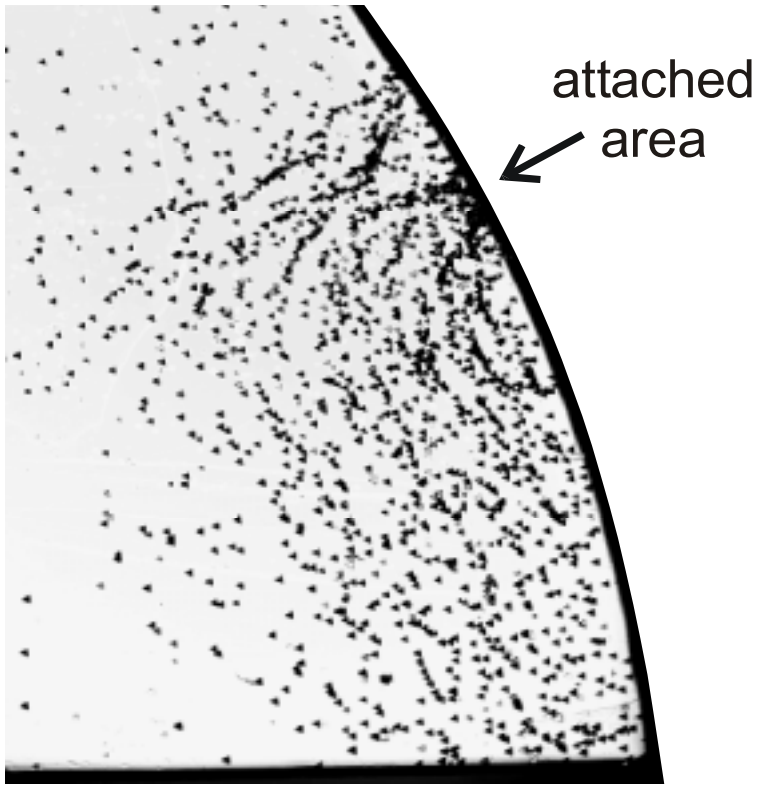
EPD ≈ 2 ·10^{4}cm^{-2}

EPD increase due to partial attachment

Detached grown slice UMC2_9



Partly attached grown slice UMC2_10



Summary

- Important thermophysical properties measurements have been made
  - –Wetting angle and surface tension of germanium melts on different substrate materials, Kaiser et al., J. Crystal Growth 231 (2001) 448-457.
  - –Wetting angles and surface tension of $Ge_{1-x}Si_x$ melts on different substrate materials, Cröll et al., J. Crystal Growth 242 (2002) 45-54.
- Substantial insight has been gained into reproducibly achieving detached Bridgman growth
  - –Bridgman growth of detached GeSi crystals, Volz et al., J. Crystal Growth 237-239 (2002) 1844-1848.
  - –Stability of detached-grown germanium single crystals, Schweizer et al., J. Crystal Growth 237-239 (2002) 2107-2111.
- Detached growth shows a two order of magnitude decrease in EPD in germanium
  - –Defect density characterization of detached-grown germanium crystals, Schweizer et al., J. Crystal Growth, 235 (2002) 161-166

RDGS Project Team

Reduction of Defects in Germanium-Silicon (RDGS)

P.I.: Dr. Frank R. Szofran, NASA/MSFC

Project Manager: Mr. Michael Purvey
Project Engineer: Mr. Richard Holmes

Proposal Team

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Co-Investigators:

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Additional RDGS Personnel

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Ms. Natalie Kaiser, Kristallographisches Institut, Freiburg, Germany

Mr. Uwe Kerat, Kristallographisches Institut, Freiburg, Germany

Ms. Penny Pettigrew, Morgan Research/MSFC

Dr. Markus Schweizer, USRA/MSFC (now at Schott Glas, Mainz)

Technical Support

C. Bahr/D. Lovell/J. Quick, Morgan Research/MSFC

P. Carpenter, USRA/MSFC

S. Gallop, Tec-Masters/MSFC

RDGS—an International Collaboration

RDGS and a parallel flight experiment in Germany (also known as RDGS) form a collaborative effort in which responsibilities and results are shared but no funds are exchanged.

- **Scientifically a single investigation**
- **Resources for German and US parts of team provided independently by DLR[1] and NASA, respectively**
- **Flight opportunities provided by NASA and ESA[2]**
- **Lead organization in US is the Marshall Space Flight Center (MSFC) and in Germany is the Kristallographisches Institut der Universität Freiburg (KI)**
- **Investigation responsibilities divided according to experience and laboratory capabilities—float zone in Germany and Bridgman growth in the US**
- **Frequent interaction by teleconferencing and visiting**

1. Deutsches Zentrum für Luft- und Raumfahrt. 2. European Space Agency

Overview of Previous Detached Growth Results

•Microgravity experiments have yielded detached ingots that have one or more of the following characteristics (Regel and Wilcox, Microgravity Science and Technology, 1999):

- •Free movement in container after growth
- •Isolated surface voids or bubbles
- •Surface ridges and lines
- •Contact only at peaks of grooved ampoules
- •Gap of 1-60 µm between ingot and wall after accounting for thermal contraction
- •Large gap (>1 mm) with a wavy surface or hourglass-shaped neck next to seed

•Occurrence of detachment is unpredictable (Regel and Wilcox, Microgravity Science and Technology, 1999):

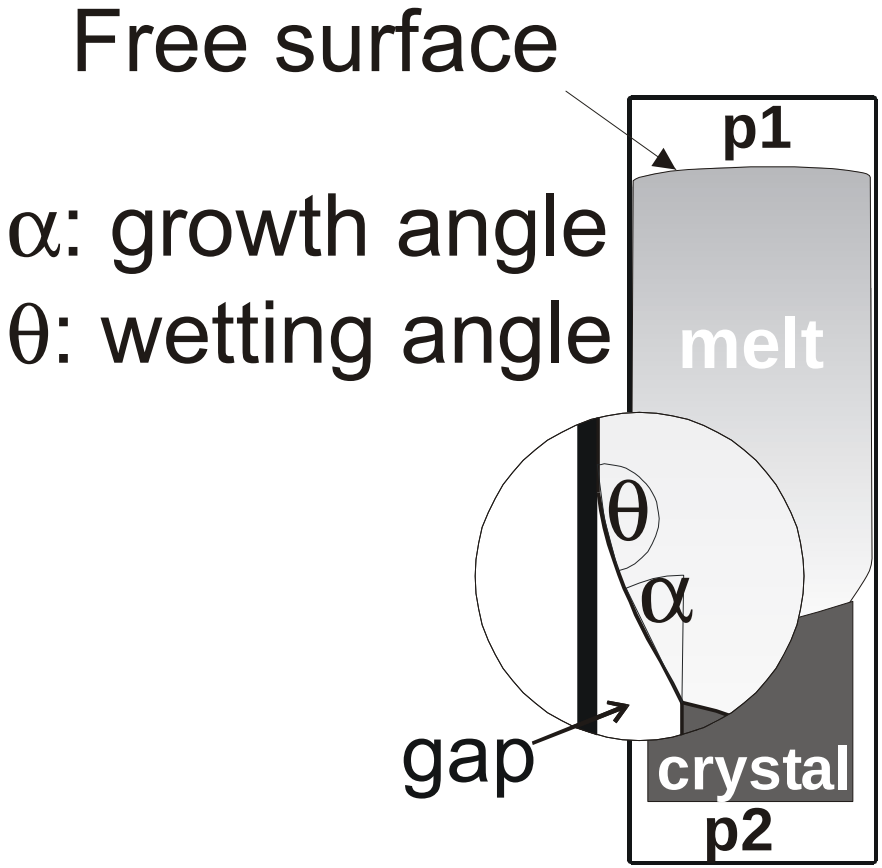
- •Predominately observed in semi-conductors but also in metals and alloys
- •Occurs at fast and slow growth rates
- •Independent of dopant
- •Features of detachment not reproducible
- •Occurrence of detachment not reproducible
- •Independent of oxygen presence

Primary Theories of Detachment

- **Free volumes and voids:**
  - **A number of configurations are energetically stable including bubbles attached to crucible (Sen and Wilcox, JCG, 1986)**
  - **Detachment based on release of gas between crucible and sample at solid-liquid interface (Regel and Wilcox, Microgravity Science and Technology, 1995)**
- **Necking (Initial large reduction in ingot diameter (Zemskov, Fiz. Khim. Obrab. Mater. (1983)):**
  - **Liquid is drawn away from the crucible if the sum of the growth angle and the wetting angle was greater than 180°**
- **Dewetting (Detachment between ridges (Duffar et. al. JCG, 1997)):**
  - **Surface phenomena such as chemical and thermal compatibility, surface state, residual cartridge atmosphere, existence of free meniscus, and internal shape of crucible (sharp angles) are important**
  - **For high contact angles, detachment occurs due to slight pollution by residual gas**
  - **For low contact angles, need high pressure difference between hot and cold regions to maintain a stable gap thickness**
- **Pressure Differential (Duffar et. al. JCG 2000)**
  - **A small meniscus at wall close to solid-liquid interface is established and controlled by controlling pressure in the gap below the liquid**
  - **Large enough pressure to balance hydrostatic head**
  - **Low enough to prevent bubbling through the liquid**

How Microgravity Will Help—Detached Bridgman

- **Larger (p2-p1) increases stability of detachment, allows experiments with more materials**
  - **Limited on Earth by bubbling**
- **Determine the role of convection in promoting detachment via the release of gas into the gap**



Selected Ampoule/Liner Materials for $Ge_{1-x}Si_x$ and Ge

pBN	Fused quartz
+ High wetting angle (160°-170°)	– *Low wetting angle (100°-130°)*
+ No significant decrease of wetting angle over time	– *Reduction of wetting angle with time*
+ Large areas grow detached in closed bottom containers even without temperature inversion	+ Partial detached growth has been achieved in a few cases
+ No sticking of the sample, even of attached parts	– *Crystal parts grown attached initially stick to ampoule,ampoule cracks*
+ Lower dislocation density than fused quartz	– *High dislocation density in attached parts*
– *Tendency for polycrystalline growth*	+ Usually single crystalline growth
– *Boron contamination (10^{17}-10^{18}cm^{-3}) leads to p-type material*	+ No electrically active doping by contamination from the crucible

Effects of Traveling Magnetic Field on Dynamics of Solidification

Dr. Konstantin Mazuruk

ABSTRACT

The Lorentz body force induced in electrically conducting fluids can be utilized for a number of material processing technologies. An application of strong static magnetic fields can be beneficial for damping convection present during solidification. On the other hand alternating magnetic fields can be used to reduce as well as to enhance convection. However, only special types of time dependent magnetic fields can induce a non-zero time averaged Lorentz force needed for convection control. One example is the rotating magnetic field. This field configuration induces a swirling flow in circular containers. Another example of a magnetic field configuration is the traveling magnetic field-TMF. It utilizes axisymmetric magnetostatic waves. This type of field induces an axial recirculating flow that can be advantageous for controlling axial mass transport, such as during solidification in long cylindrical tubes. Incidentally, this is the common geometry for crystal growth research. The Lorentz force induced by TMF can potentially counter-balance the buoyancy force, diminishing natural convection, or even setting up the flow in reverse direction. Crystal growth process in presence of TMF can be then significantly modified. Such properties as the growth rate, interface shape and macro segregation can be affected and optimized. Melt homogenization is the other potential application of TMF. It is a necessary step prior to solidification. TMF can be attractive for this purpose, as it induces a basic flow along the axis of the ampoule. TMF can be a practical alloy mixing method especially suited for a solidification research in space. In the theoretical part of this work, calculations of the induced Lorentz force in the whole frequency range have been completed. The basic flow characteristics for the finite cylinder geometry are completed and first results on stability analysis for higher Reynolds numbers are obtained. A theoretical model for TMF mixing is also developed. In the experimental part, measurements of flow induced by TMF in a column of Mercury are presented. Also, an alloy mixing of Bi-Sn of the eutectic composition is demonstrated. A traveling magnetic field of 4mT at 3kHz applied for 120 min. is found to be sufficient to homogenize an alloy enclosed in a 1cm diameter and 12 cm long tube.

Effects of Traveling Magnetic Field on Dynamics of Solidification

Dr. Konstantin Mazuruk, Universities Space Research Association
Dr. Richard Grugel, MSFC/NASA

Objectives of this work:

- to develop theoretical and experimental fundamental features of the traveling magnetic field (TMF) technique, with the aim of identifying its benefits for microgravity research on solidification processing

- to determine the influence of a traveling magnetic field on the following selected technologies:
  - crystal growth of semiconductor materials by Bridgeman and Float Zone techniques
  - mixing of metal alloy melts prior to solidification

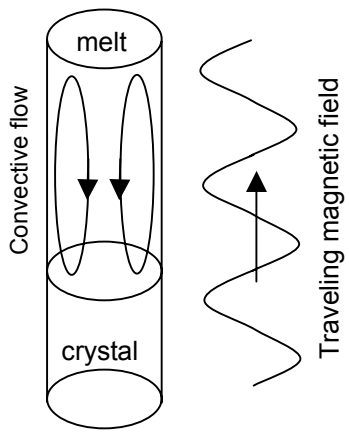
Effects of Traveling Magnetic Field on Dynamics of Solidification

Konstantin Mazuruk, Universities Space Research Association

Not well-explained convective flows adversely affect quality control of semiconductor crystal growth

Why:

• On earth, thermal and solutal gradients induce unsteady convection in the melt from which the crystal is grown. Unsteady convection degrades the homogeneity and increases the defect concentration in grown materials. Controlling convection is the primary goal to improve semiconductor crystals



How:

• Buoyancy force can be counter-balanced by the Lorentz force induced by the traveling magnetic field. Thus, the resulting driving force can be significantly smaller. Consequently, the convective flow can be substantially reduced

Impact:

• The highest quality semiconductor crystals are required for fabrication of novel optical and electronic high-speed devices. The proposed technique can help to achieve this goal.

"An exciting new approach to control of convection in semiconductor melts is proposed in the present research. If successful, this work will define a new state-of-the-art for convection in semiconductor crystal growth." ATP Letter, January 2000

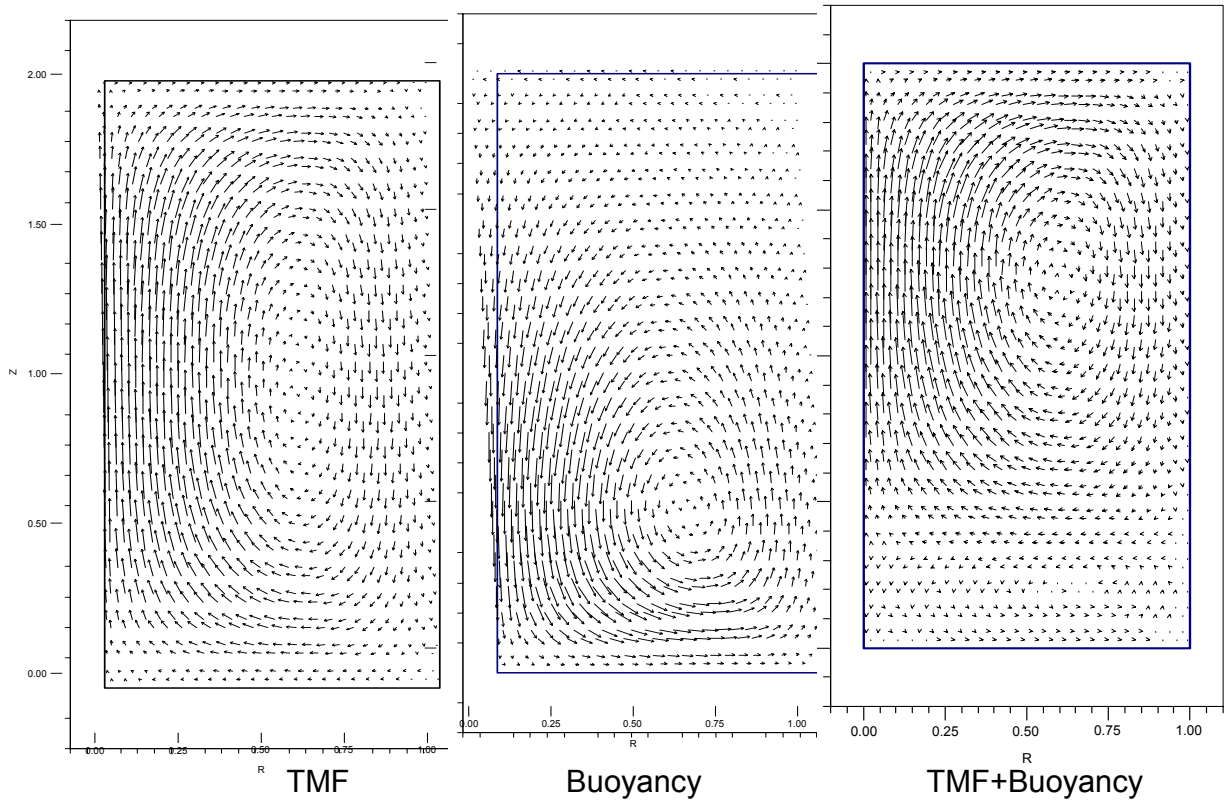
Effects of Traveling Magnetic Field on Dynamics of Solidification

Traveling magnetic field **(TMF) is based on imposing a controlled phase-shift in a train of electromagnets, forming a stack. Thus, the induced magnetic field can be considered to be traveling along the axis of the stack. The coupling of this traveling magnetostatic wave with an electrically conducting fluid induces the time independent body Lorentz force which sets up a basic flow in a form of a single axisymmetric roll. The magnitude and direction of this flow can be remotely controlled. Furthermore, it is possible to localize the effect of this force field through activating only a number of the magnets. This force field generated in the fluid can, in principle, be used to control and modify convection in the molten material. For example, it can be used to enhance convective mixing in the melt, and thereby modify the interface shape, and macrosegregation. Alternatively, it can be used to counteract thermal and/or solutal buoyancy forces. High frequency TMF can be used in containerless processing techniques such as float zoning, to affect the very edge of the fluid so that Marangoni flow can be counter balanced.**

Effects of Traveling Magnetic Field on Dynamics of Solidification

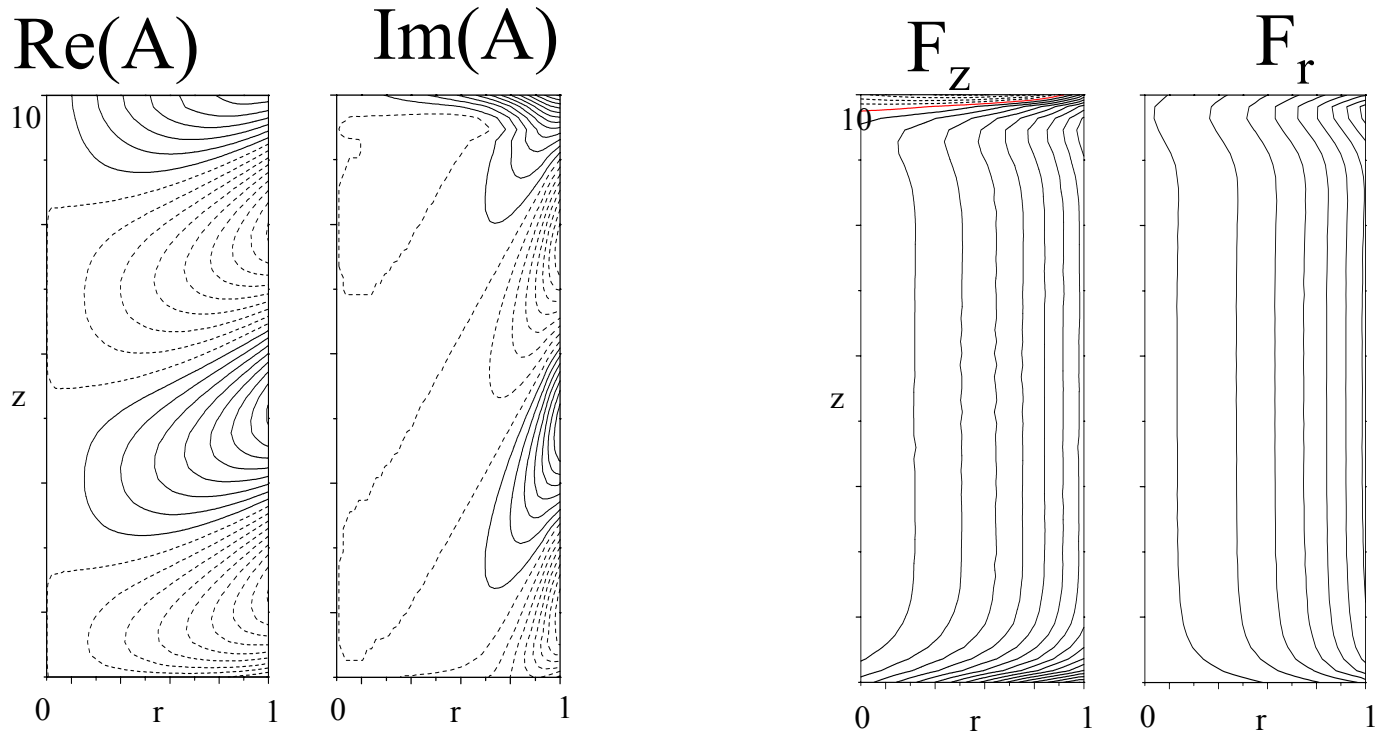
Control of fluid flow by TMF

In a molten cylindrical zone, traveling magnetic fields induce a body Lorentz force which can be set in the direction opposite to that of a buoyancy force. A stagnant convective region near the growing crystal can be obtained.



Flow patterns generated by a TMF, buoyancy, and a TMF and buoyancy combined.

Lorentz Force for Finite Cylinders



For high frequencies, a delay of the magnetic wave is observed in the medium, as seen above from the snapshot of the vector potential. The resulting Lorentz force displays sharp variations at the end cups of the cylinder.

Re(A) is the real part of the vector potential. Im(A) is the imaginary part of the vector potential. F_z is the z-component of the Lorentz force. F_r is the r-component of the Lorentz force.

Time independent Lorentz force induced by a stack of two circular coils

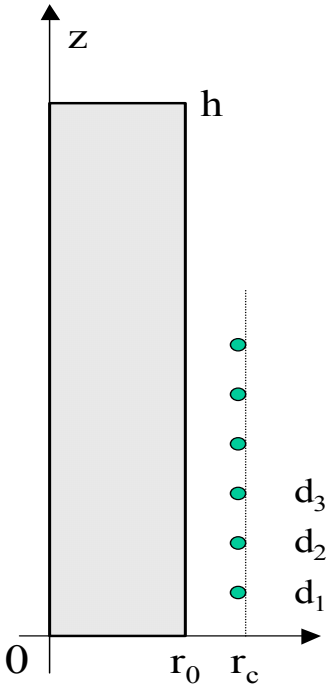


Fig.1 Schematic of the cell with several coils displayed

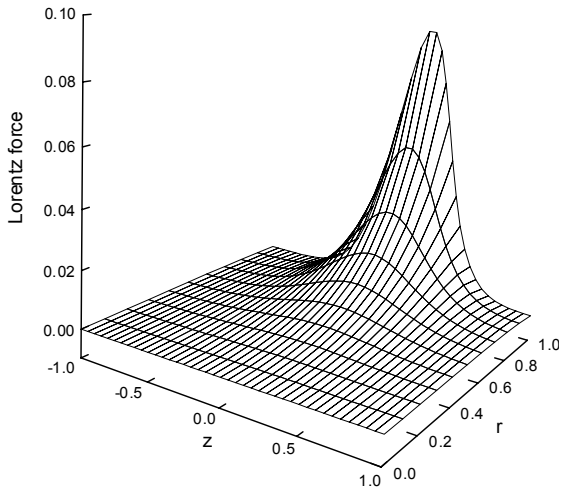


Fig.2. Non-dimensional Lorentz force induced by two circular coils

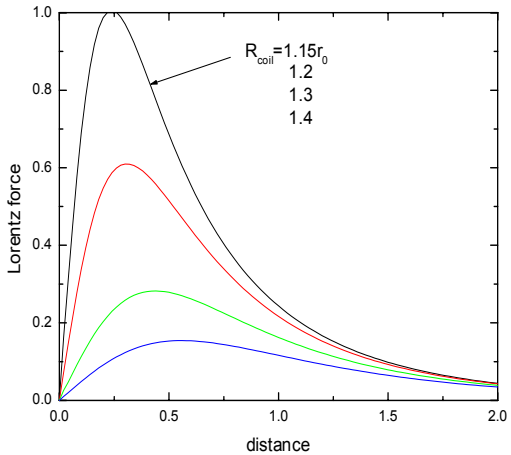
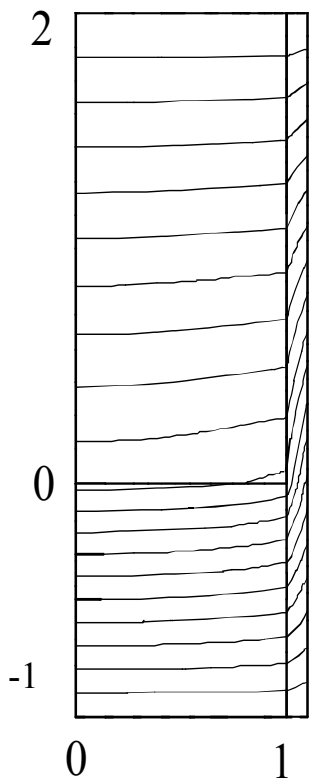
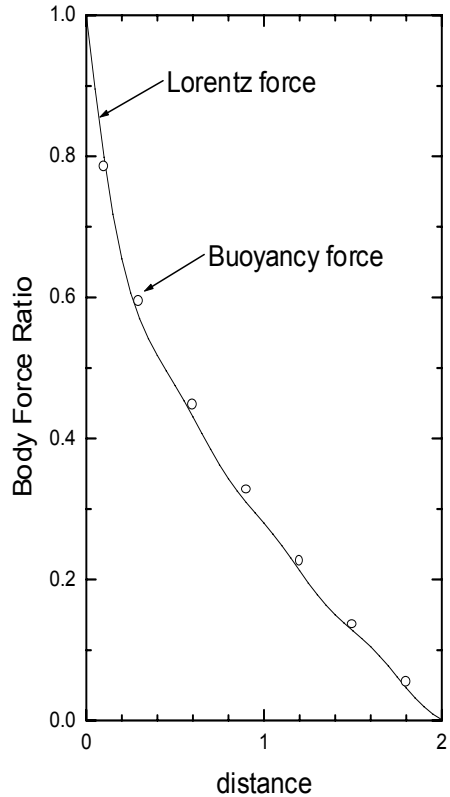


Fig.3. Non-dimensional Lorentz force as a function of coil separation

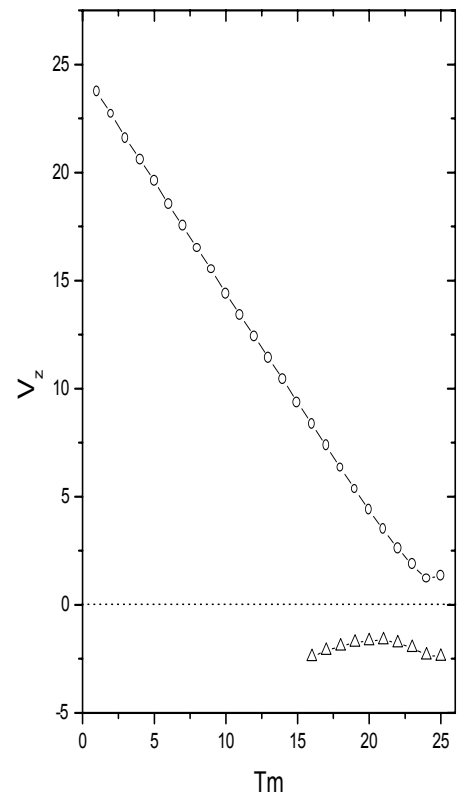
Vertical Bridgman with TMF



VB configuration with isotherms



Buoyancy and adopted Lorentz force as a function of z



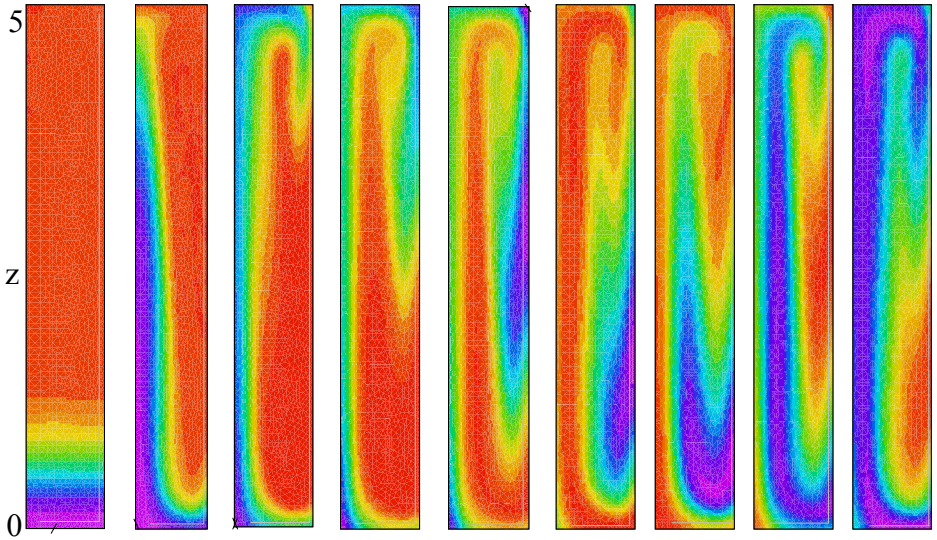
Maximum an minimum values of V_z as a function of Tm

12 times reduction of the global flow is obtained.

V_z is the z-component of the flow velocity and Tm is the magnetic Taylor number.

Mixing induced by TMF

Mixing induced by TMF. An initial concentration profile is radially uniform (first left). As time increases, solute homogenizes. From the left to the right the nondimensional time is increased by 0.1 step. The maximum and minimum values of solute concentration change as follows: (2.0,0.0), (1.97,0.0), (1.81, 0.0), (1.21,0.0), (0.68, 0.02), (0.55, 0.07), (0.49, 0.11), (0.44, 0.15), (0.39, 0.18).



Experiments with mixing by TMF

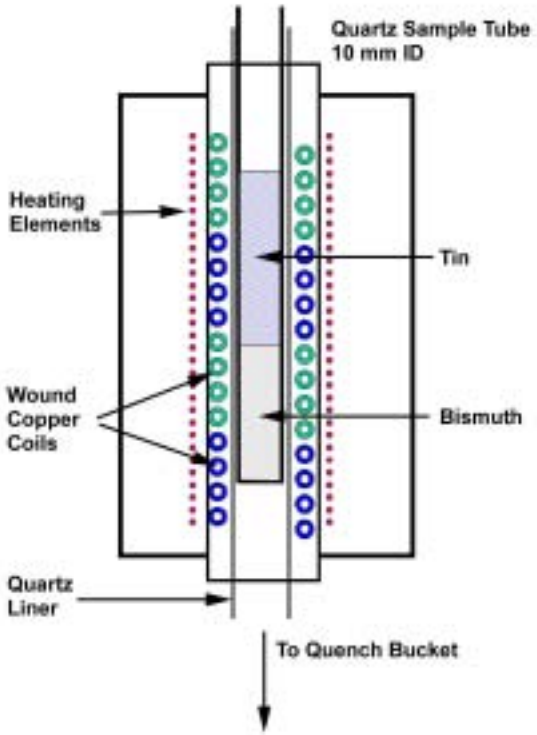
In an attempt to verify the mixing predictions a coil arrangement was constructed and placed in a tube furnace, a quartz liner was then inserted into the coil to align the sample tube. The sample to be tested consisted of a ~10mm diameter cylinder of pure bismuth (density = 9.8gcm^{-1}) upon which sat a ~10mm diameter cylinder of pure tin (density = 7.3gcm^{-1}). These cylinders were placed in a 10mm ID quartz tube, the lengths (weights) calculated, if fully mixed upon melting, to result in a cylinder ~13cm in length having a eutectic composition. A coating of boric acid was placed between the ingots to facilitate removing any oxides on the ingot contact surfaces.

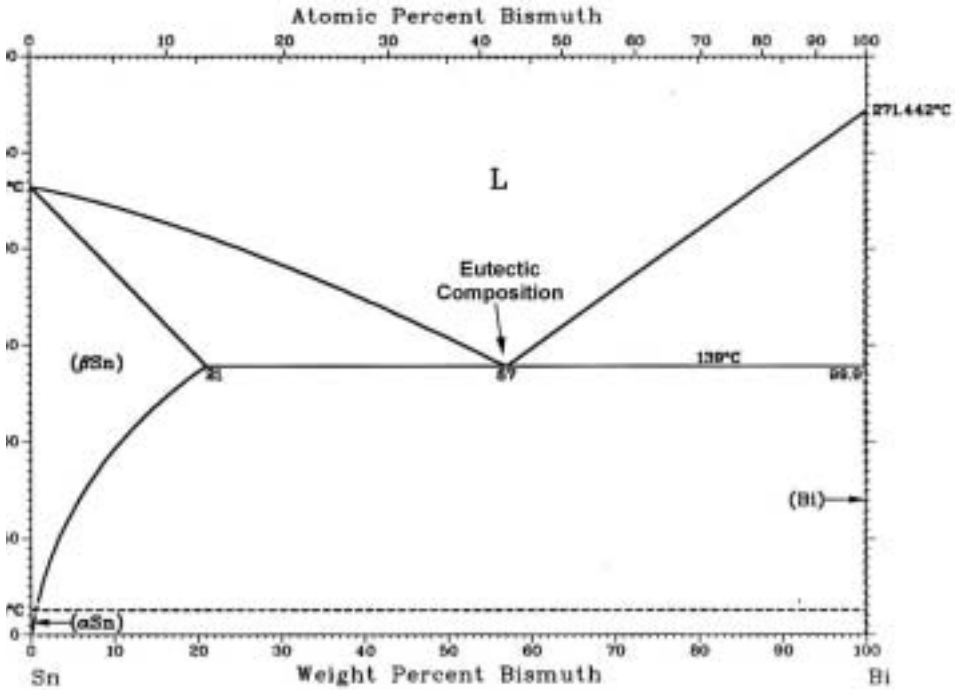
Initially, the quartz tube containing the sample was then placed in the furnace bore having a temperature of ~300°C. The sample was held for two hours; a temperature difference of ~10K was measured from the sample bottom (colder) to the top. After soaking in the furnace the molten sample was rapidly quenched by dropping it into a bucket of ice water. A second sample was identically processed but in conjunction with the applied Traveling Magnetic Field.

Mixing by natural convection/diffusion was insufficient for the given time to promote complete mixing.

Experiments with mixing by TMF

Schematic Representation of the Furnace Assembly used in this Investigation

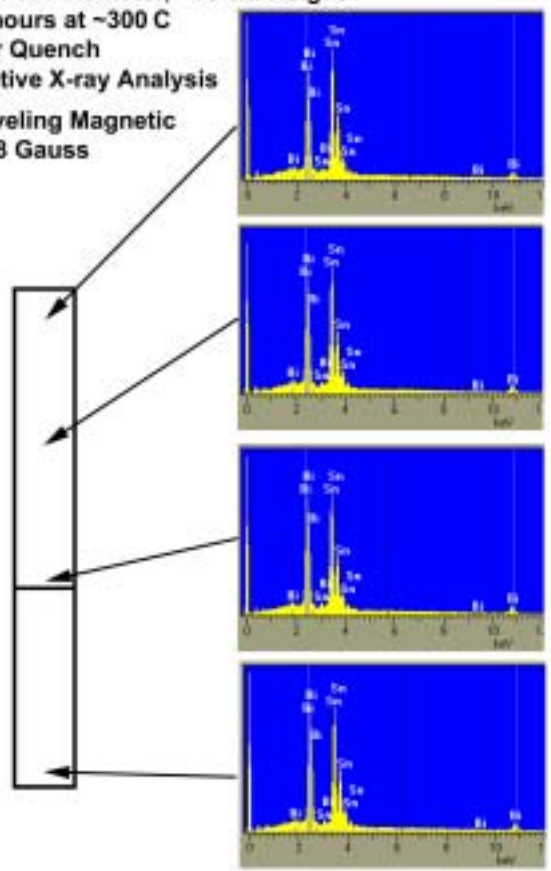




Experiments with mixing by TMF

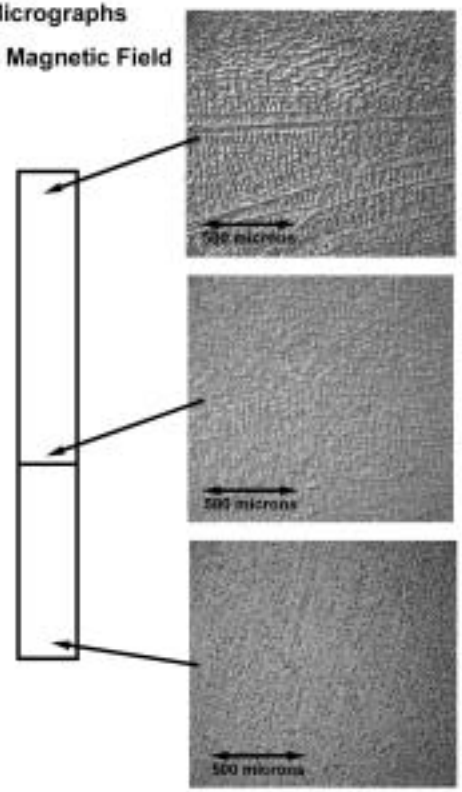
Sn - Bi "Eutectic Mixture"
Sample: 1 cm Diameter, ~13 cm Height
Held ~2 hours at ~300 C
Ice Water Quench
Comparative X-ray Analysis

With Traveling Magnetic Field ~38 Gauss



Sn - Bi "Eutectic Mixture"
Sample: 1 cm Diameter, ~13 cm Height
Held ~2 hours at ~300 degree C
Ice Water Quench
Longitudinal Micrographs

With Traveling Magnetic Field ~38 Gauss

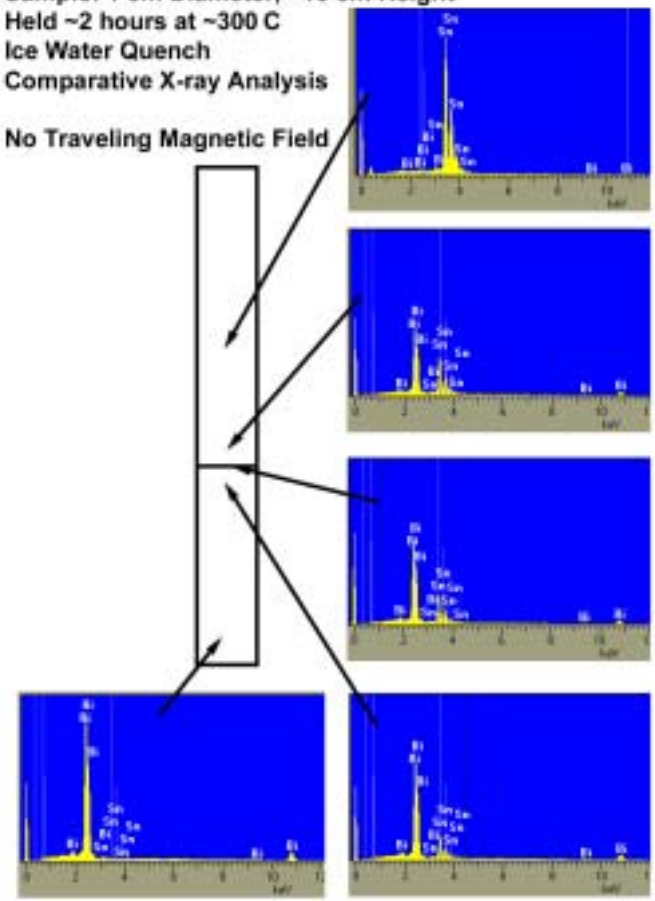


Effects of Traveling Magnetic Field on Dynamics of Solidification

Experiments with mixing by TMF

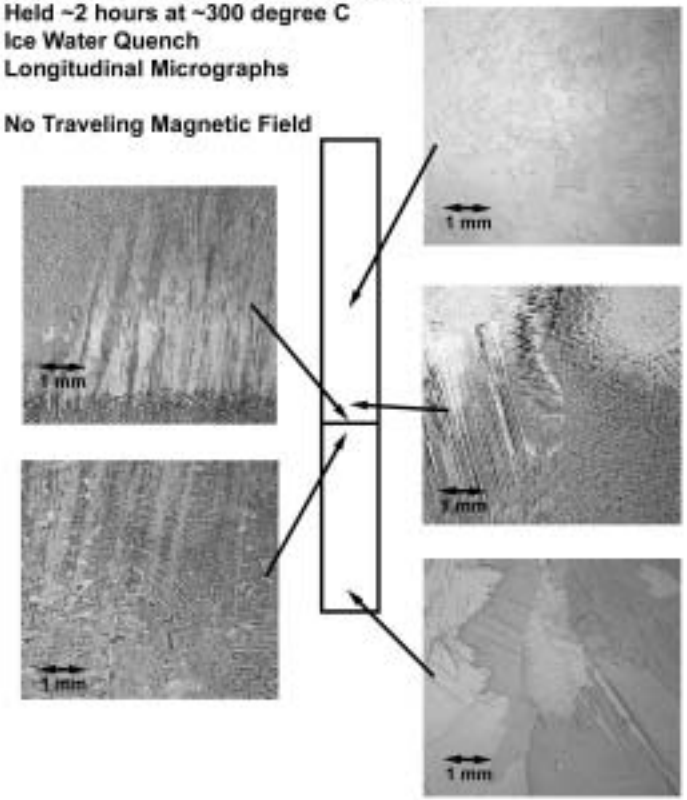
Sn - Bi "Eutectic Mixture"
Sample: 1 cm Diameter, ~13 cm Height
Held ~2 hours at ~300 C
Ice Water Quench
Comparative X-ray Analysis

No Traveling Magnetic Field



Sn - Bi "Eutectic Mixture"
Sample: 1 cm Diameter, ~13 cm Height
Held ~2 hours at ~300 degree C
Ice Water Quench
Longitudinal Micrographs

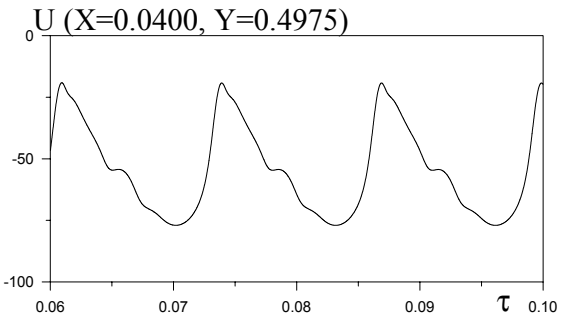
No Traveling Magnetic Field

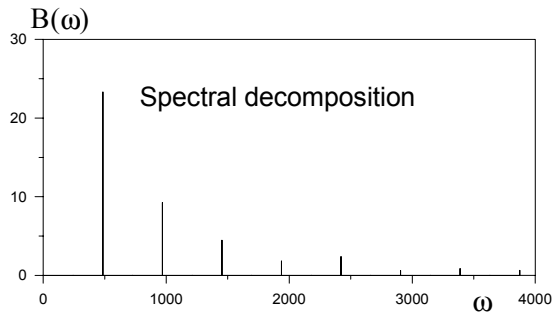


modeling: The flow patterns during the period ($\tau^* \approx 0.013$)

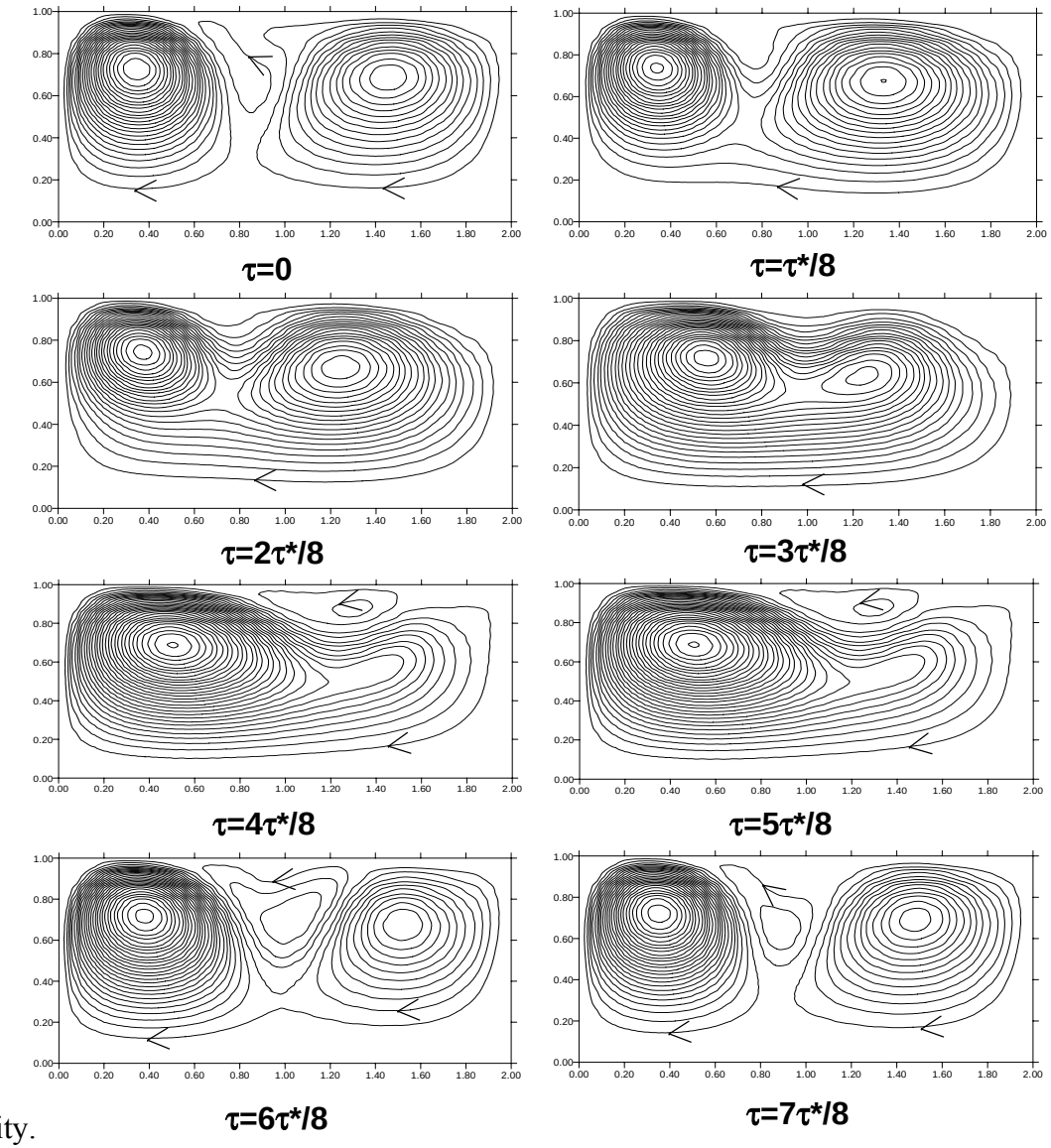
At high excitations, a periodic flow is induced. Flow pattern in the cylinder of the aspect ratio of 2 and for the value of the non-dimensional driving force represented by the magnetic Taylor number of 10^6

Horizontal velocity component at a specific position as a function of time



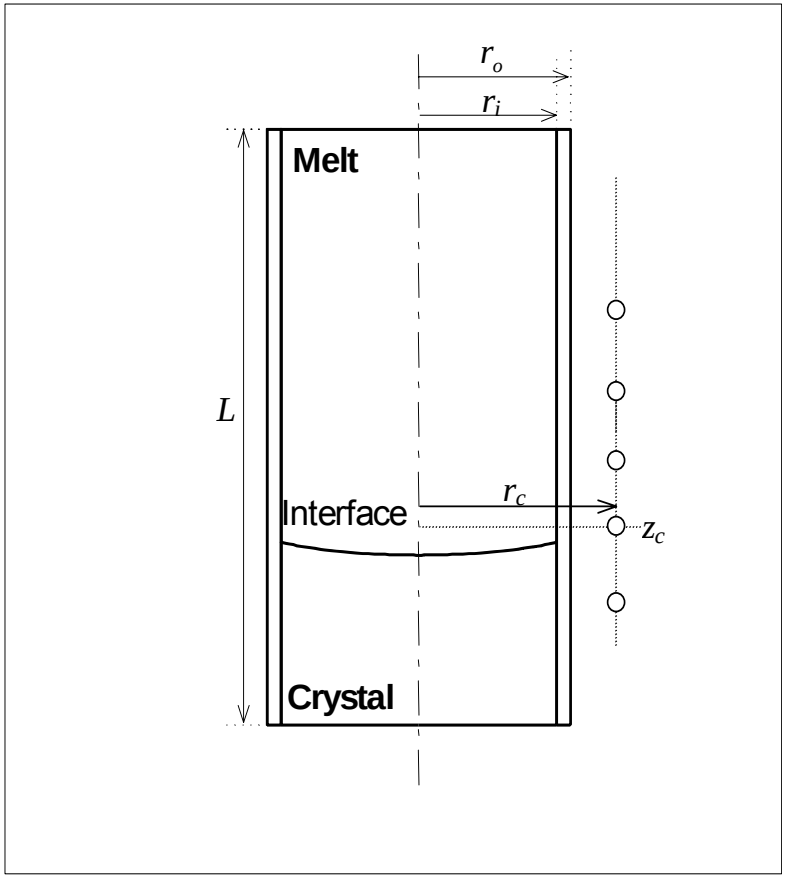


Where B(ω) is the power spectrum of the flow velocity.

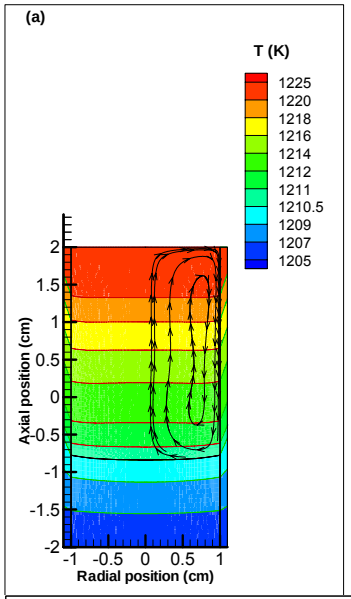


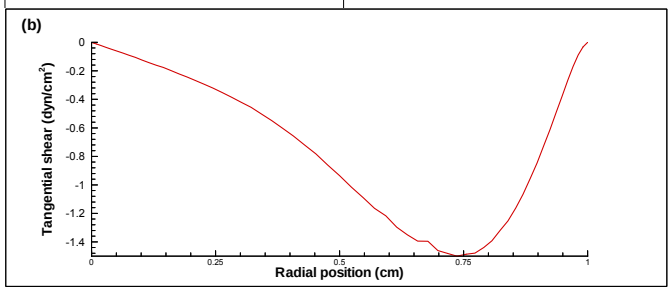
Effects of Traveling Magnetic Field on Dynamics of Solidification

Modeling of Bridgman growth of Ge



Geometry of the Bridgman growth of Ge used in simulations





Buoyancy-only melt convection and temperature profile (a), and tangential shear at the interface (b): Gr = .94 × 10^5, Re = .115× 10^4.

List of properties and dimensions used in simulations

Density, $\rho^{(1,2)}$ (g/cm^3) 5.5, 5.5

Thermal conductivity, $k^{(1,2,3)}$ (W/cm-K) 0.39, 0.17, .028

Specific heat, $c_p^{(1,2)}$ (J/g-K) 0.39,0.39

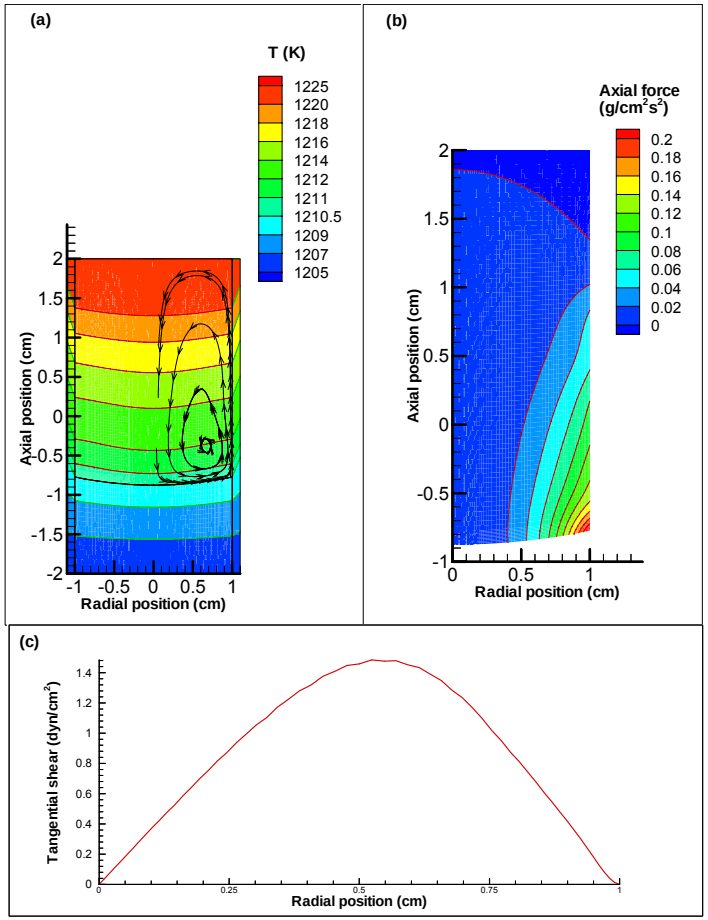
Electrical conductivity, $\sigma^{(1,2)}$ (S/cm) 1.5×10^4

dT/dz (K/cm) 5

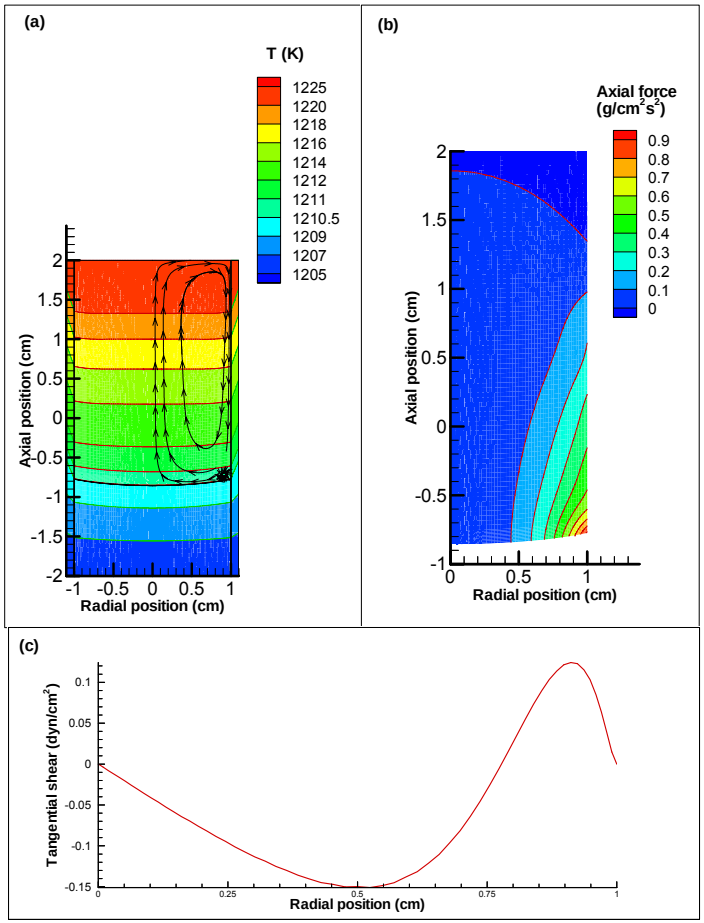
r_i, r_o (cm) 1.0, 1.1

Effects of Traveling Magnetic Field on Dynamics of Solidification

Modeling of Bridgman growth of Ge



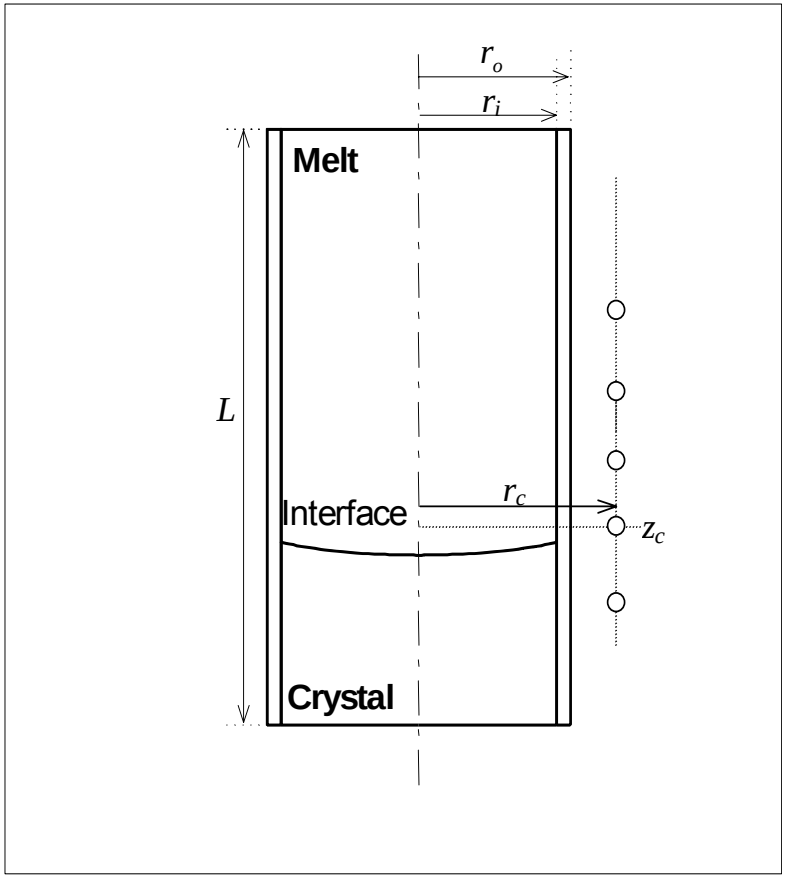
TMF-only melt convection and temperature contours (a), TMF-induced axial force (b), and tangential shear at the interface (c): Tm = .17× 10^7, Re = .114 × 10^4. Re has the same magnitude as the one displayed in Figure 7.



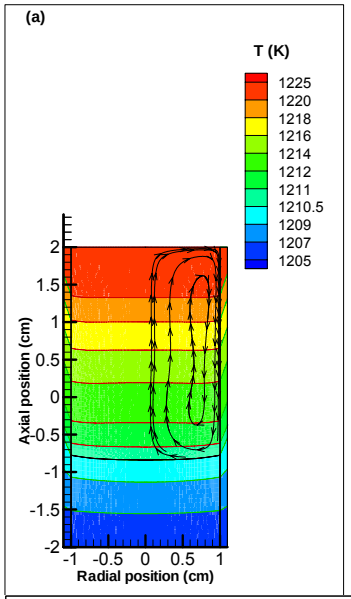
Buoyancy and TMF convection and temperature contours (a); TMF-induced axial force (b); and tangential shear at the interface (c): Gr = 1.2 × 10^6, Tm = .64 × 10^7, Re = .116 × 10^3.

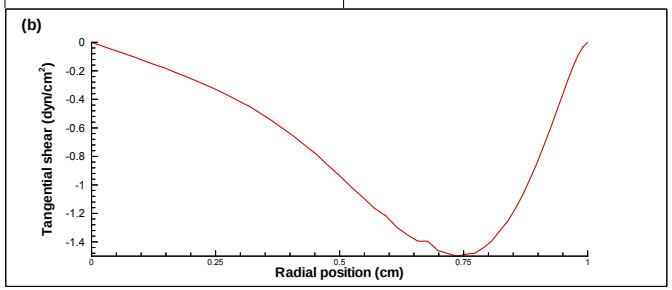
Effects of Traveling Magnetic Field on Dynamics of Solidification

Modeling of Bridgman growth of Ge



Geometry of the Bridgman growth of Ge used in simulations





Buoyancy-only melt convection and temperature profile (a), and tangential shear at the interface (b): Gr = $.94 \times 10^5$, Re = $.115\times 10^4$.

List of properties and dimensions used in simulations

Density, $\rho^{(1,2)}$ (g/cm^3) 5.5, 5.5

Thermal conductivity, $k^{(1,2,3)}$ (W/cm-K) 0.39, 0.17, .028

Specific heat, $c_p^{(1,2)}$ (J/g-K) 0.39,0.39

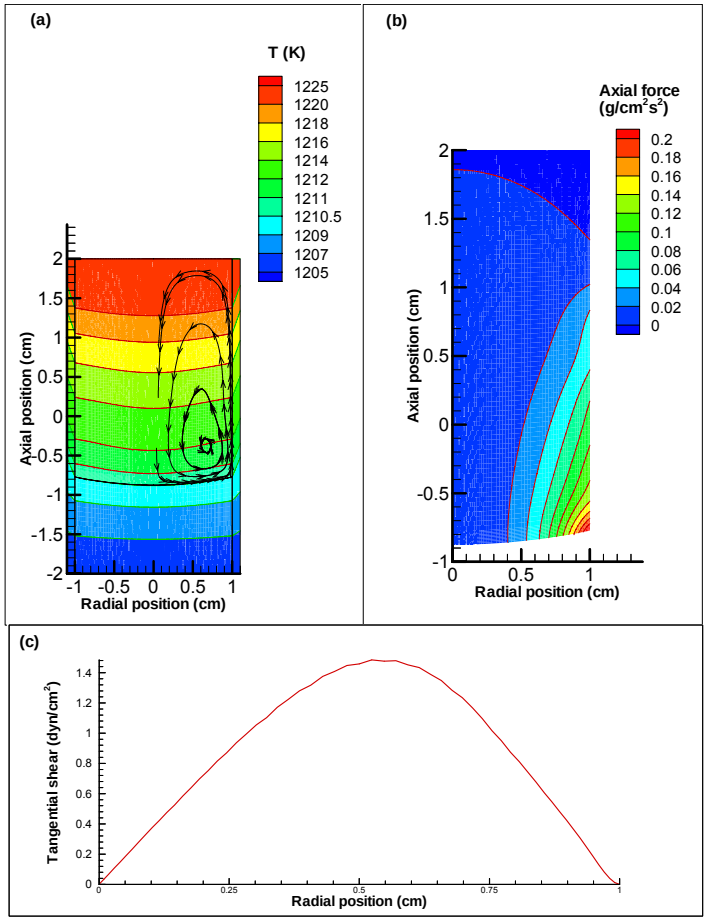
Electrical conductivity, $\sigma^{(1,2)}$ (S/cm) 1.5×10^4

dT/dz (K/cm) 5

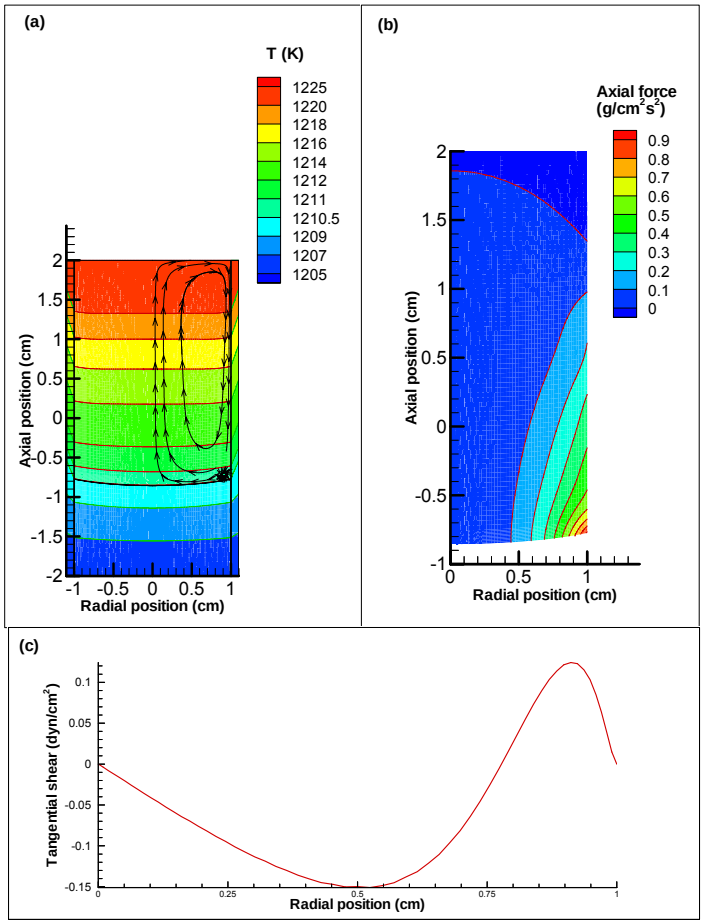
r_i, r_o (cm) 1.0, 1.1

Effects of Traveling Magnetic Field on Dynamics of Solidification

Modeling of Bridgman growth of Ge



TMF-only melt convection and temperature contours (a), TMF-induced axial force (b), and tangential shear at the interface (c): Tm = .17× 10^7, Re = .114 × 10^4. Re has the same magnitude as the one displayed in Figure 7.



Buoyancy and TMF convection and temperature contours (a); TMF-induced axial force (b); and tangential shear at the interface (c): Gr = 1.2 × 10^6, Tm = .64 × 10^7, Re = .116 × 10^3.

USES OF COMPUTED TOMOGRAPHY FOR CHARACTERIZING MATERIALS GROWN TERRESTRIALLY AND IN MICROGRAVITY

Gillies, Donald C. and H. Peter Engel , Wyle Labs, Kennedy Space Center, FL

Computed Tomography (CT) has proved to be of inestimable use in providing a rapid evaluation of a variety of samples from Mechanics of Granular Materials (MGM) to electronic materials (Ge-Si alloys) to space grown materials such as meteorites. The system at Kennedy Space Center (KSC), because of its convenient geographical location, is ideal for examining samples before launch and immediately after returning to Earth. It also has the advantage of the choice of fluxes, and in particular the use of a radioactive cobalt source, which is basically monochromatic. This permits a reasonable measurement of density to be made from which chemical composition can be determined. Due to the current dearth of long duration space grown materials, the CT instrument has been used (1) to characterize materials in preparation for flight, (2) to determine thermal expansion values, and (3) to examine long duration space grown materials, i.e. meteorites.

This work will first describe the establishment of the protocol for obtaining the optimum density readings for any material. Included will be the effects of the hardware or instrumental parameters that can be controlled, and the techniques used to process the CT data. Examples will be given of the compositional variation along a single crystals of Ge-Si alloy.

Density variation with temperature has been measured in preparation for future materials science experiments; this involved the fabrication at MSFC and installation of a single zone furnace at KSC incorporating a heat pipe to ensure high temperature uniformity. At the time of writing the thermal expansion of lead has been measured from room temperature to 900°C. Three methods are available. Digital radiography enables length changes to be determined. Prior to melting the sample is smaller than the container and the diameter change can be measured. Most critical, however, is the density change in solid, through the melting region, and in the liquid state. These data are needed for engineering purposes to aid in the design of containment cartridges, and for enabling fluid flow calculations. A second sample, with the lead alloyed with antimony is ready for scanning. This corresponds to the planned composition of Dr. Poirier's flight experiment. Other materials pertinent to NASA programs such as Al-Cu (Trivedi), CdTe (Banish), HgCdTe (Lehoczky) will be examined below and above the melting point.

Finally, three-dimensional results will be shown of the structure of a two-phase metallic meteorite of metal and sulfide, in which the iron-nickel phase has coarsened during slow cooling over hundreds of millions of years.

Use of Computed Tomography for Characterizing Materials Grown Terrestrially and in Microgravity

Donald C. Gillies and H. Peter Engel

NASA/MSFC Wyle/KSC

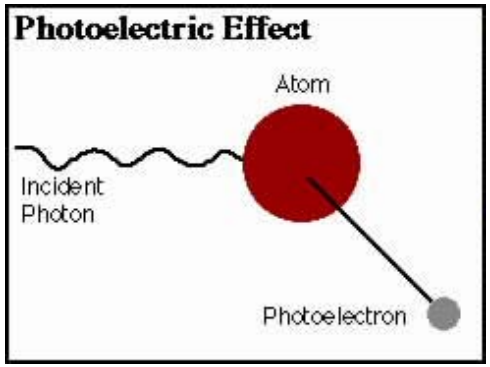
Ground-based project selected from the 1998 NRA. Continuing through September 2003

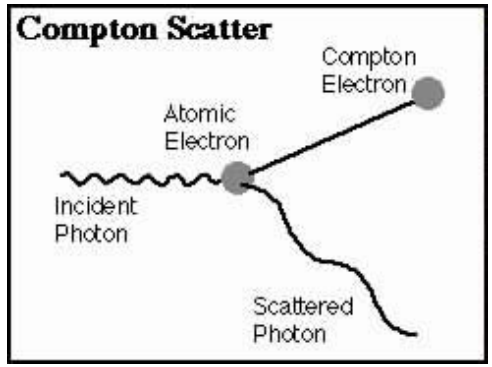
AGENDA for this Presentation

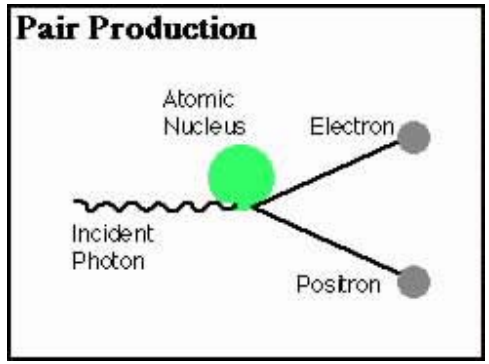
1. A little theory and background
2. Old (pre-NRA) results
3. Solid solutions (Ge-Si)
4. Thermal expansion data
5. Space grown material

Fundamental Scattering Theory

Three modes of scattering will be considered







<1 MeV

Photoelectric Effect. Total absorption of incident photon with the emission of a bound electron

0.8 - 5 MeV

Compton Scattering. Produces free electron and a scattered (less energetic) photon

>3 MeV

Pair production. Absorption of the incident photon with the creation of an electron-positron pair

$\mu_{PE} \sim K_1 Z^{4.5}/E^3$

$\mu_C \sim K_2 Z/f(E)$

$\mu_{PP} \sim K_3 Z^2 g(E)$

Note: Scattering by the Compton mechanism is directly proportional to Z, the atomic number, and so the scattering is directly proportional to the density of the material.

E is incident energy, and f and g are energy functions.

Candidates for Quantitative CT

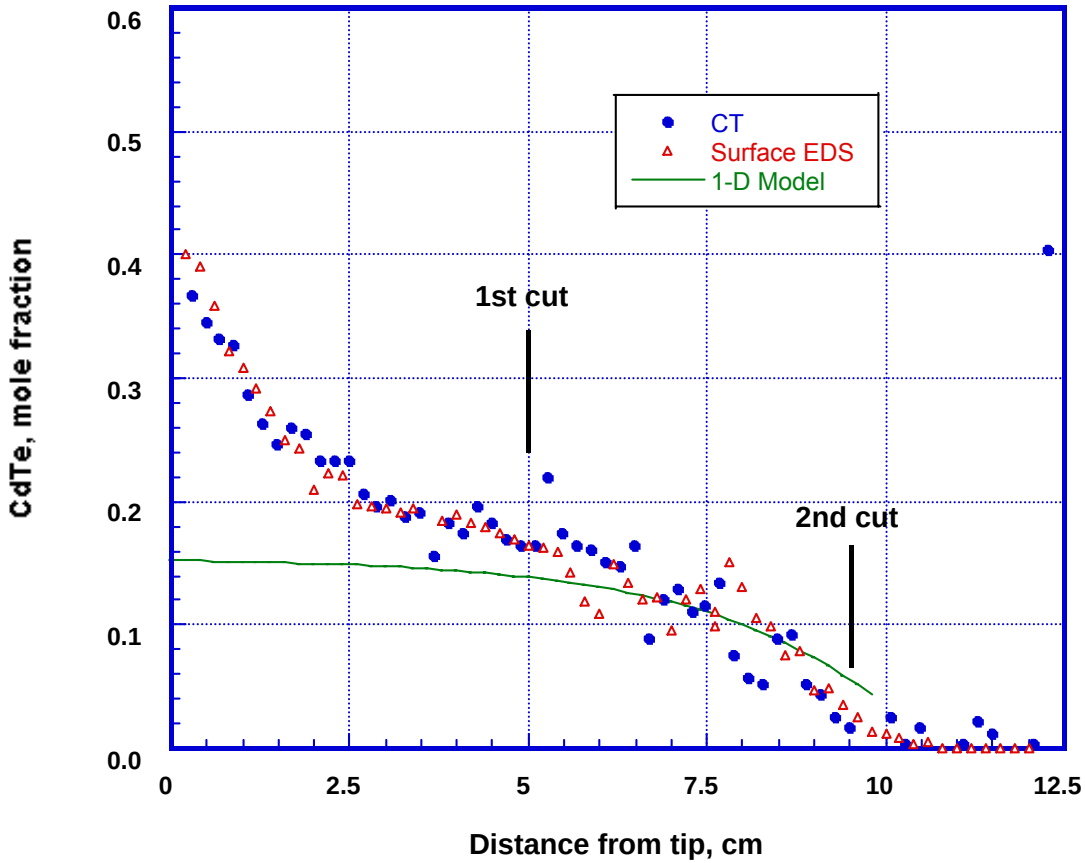
Material	Alloy 1	Alloy 2	Δ Density	PI
PbSnTe	PbTe 8.27 g/cc	SnTe 6.53 g/cc	26%	Fripp
HgCdTe	HgTe 8.112	CdTe 5.852	38%	Lehoczky
GeSi	Ge 5.325	Si 2.329	129%	Szofran
Pb-Sb	Pb 11.341	Pb/.058Sb 11.071	2.4%	Poirier
Al-Cu	Al 2.699	Al/.04Cu 2.948	9.2%	Trivedi

Mercury Cadmium Telluride Solid Solution

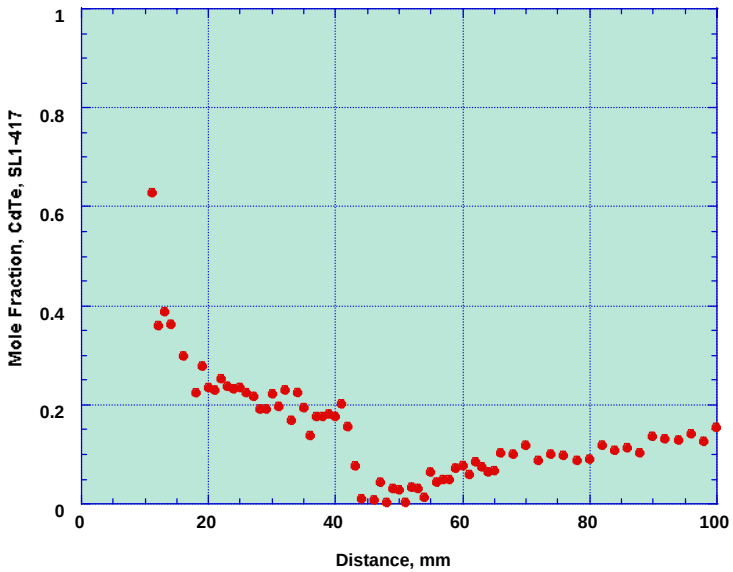
Showing:

Comparison of composition determined from CT density and energy dispersive spectrometry on the SEM.

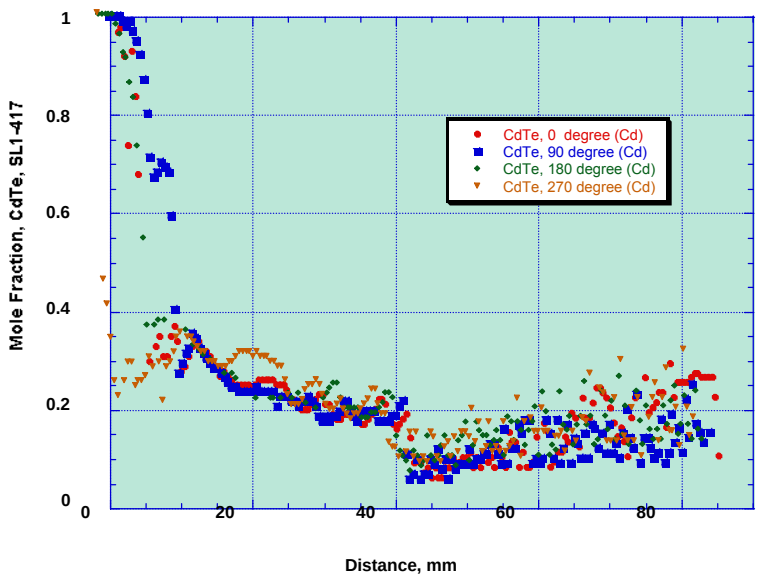
Technique proved invaluable in determining where to cut the boule.



USMP-4 Flight Sample – Composition Determination



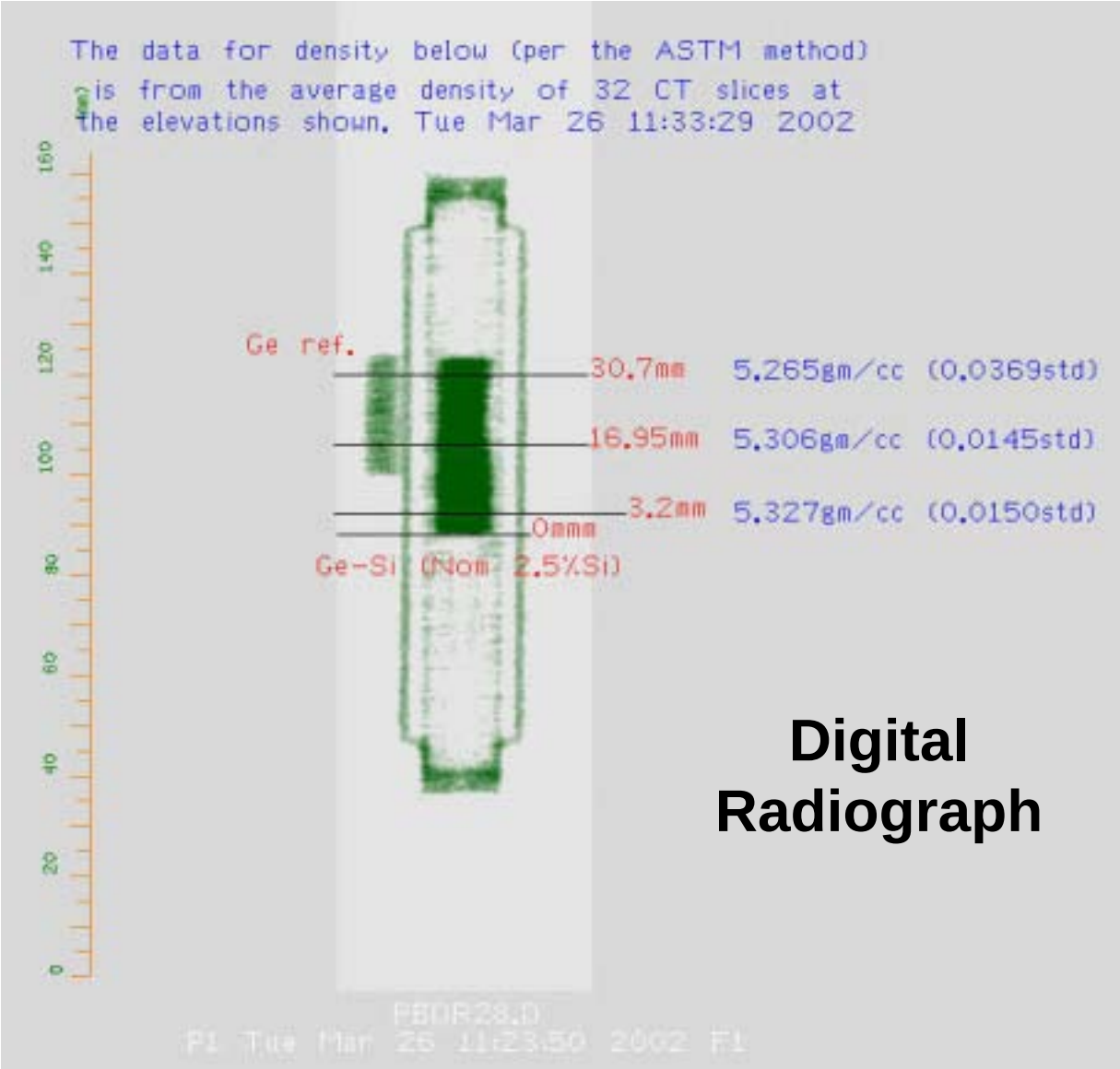
CT Data giving average composition across boule



Wavelength Dispersive Spectrometry of four surfaces

The averaging effect of the CT data is useful in assessing the composition profile, particularly after quenching (42 mm). Cutting wafers and doing density measurements would be the alternative method of getting these data.

CT of a Ge-Si Single Crystal Seed



Digital Radiograph

Results

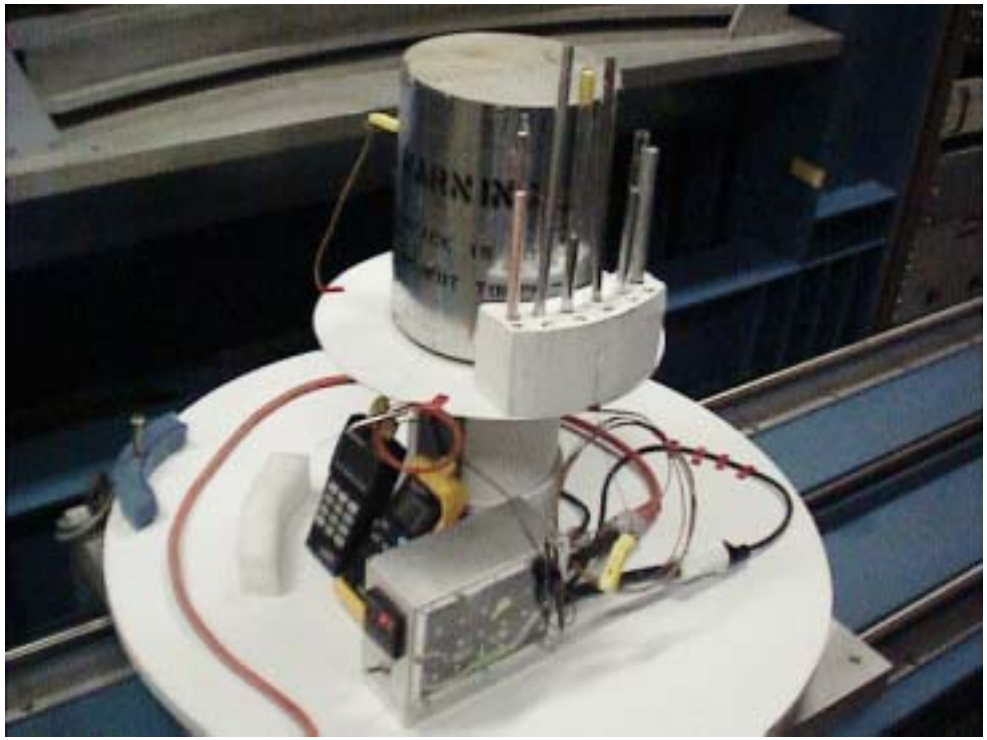
Center 2.07 wt% Si

Bottom 0.67 wt% Si

Seed crystal for Dr. Szofran's Flight Experiment

RDGS

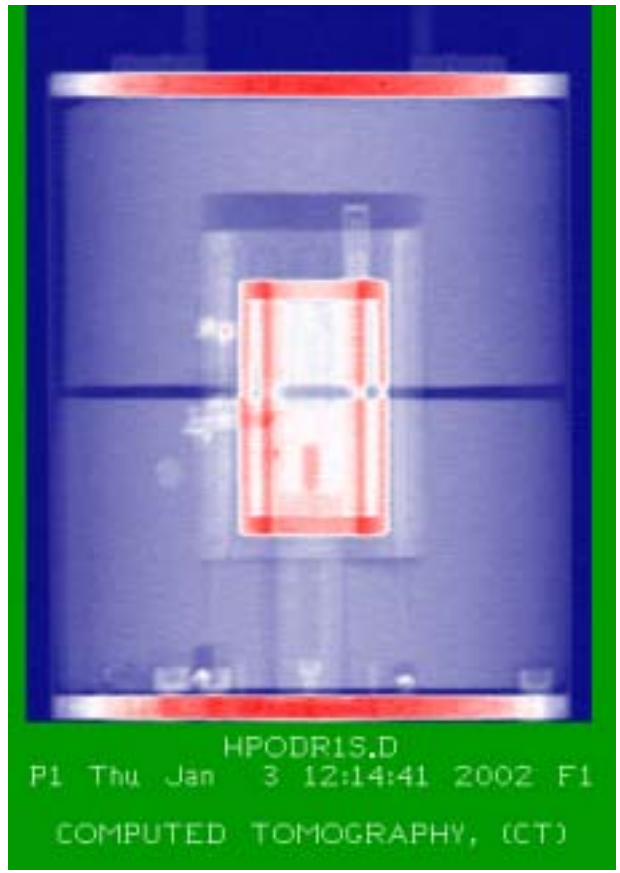
MSFC-designed and built furnace residing on the CT translation stage at KSC



Furnace is single zone with a sodium heat pipe.

Note the standards at room temperature surrounding the furnace.

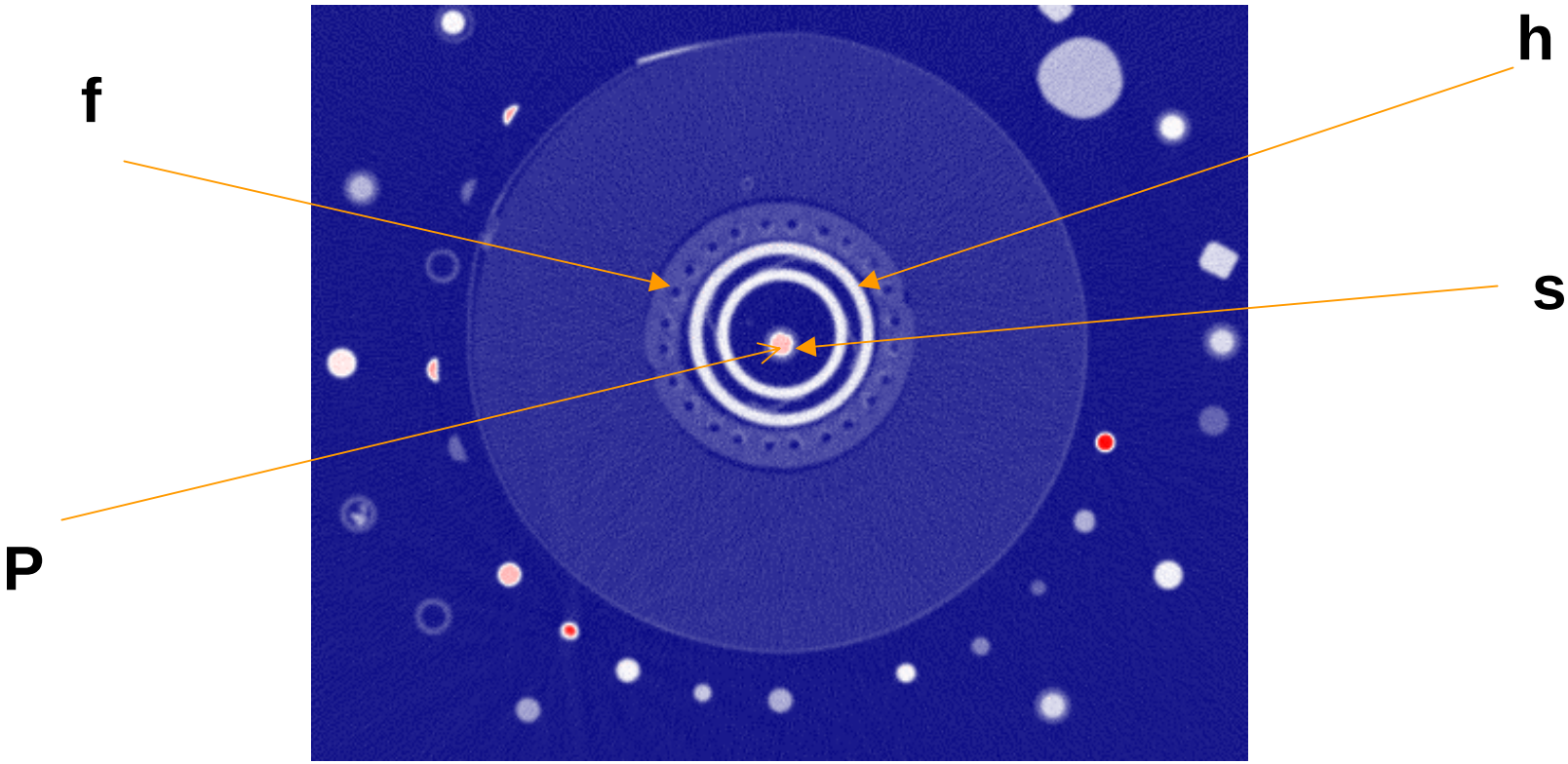
Thus far Ga, In and Pb have been examined.



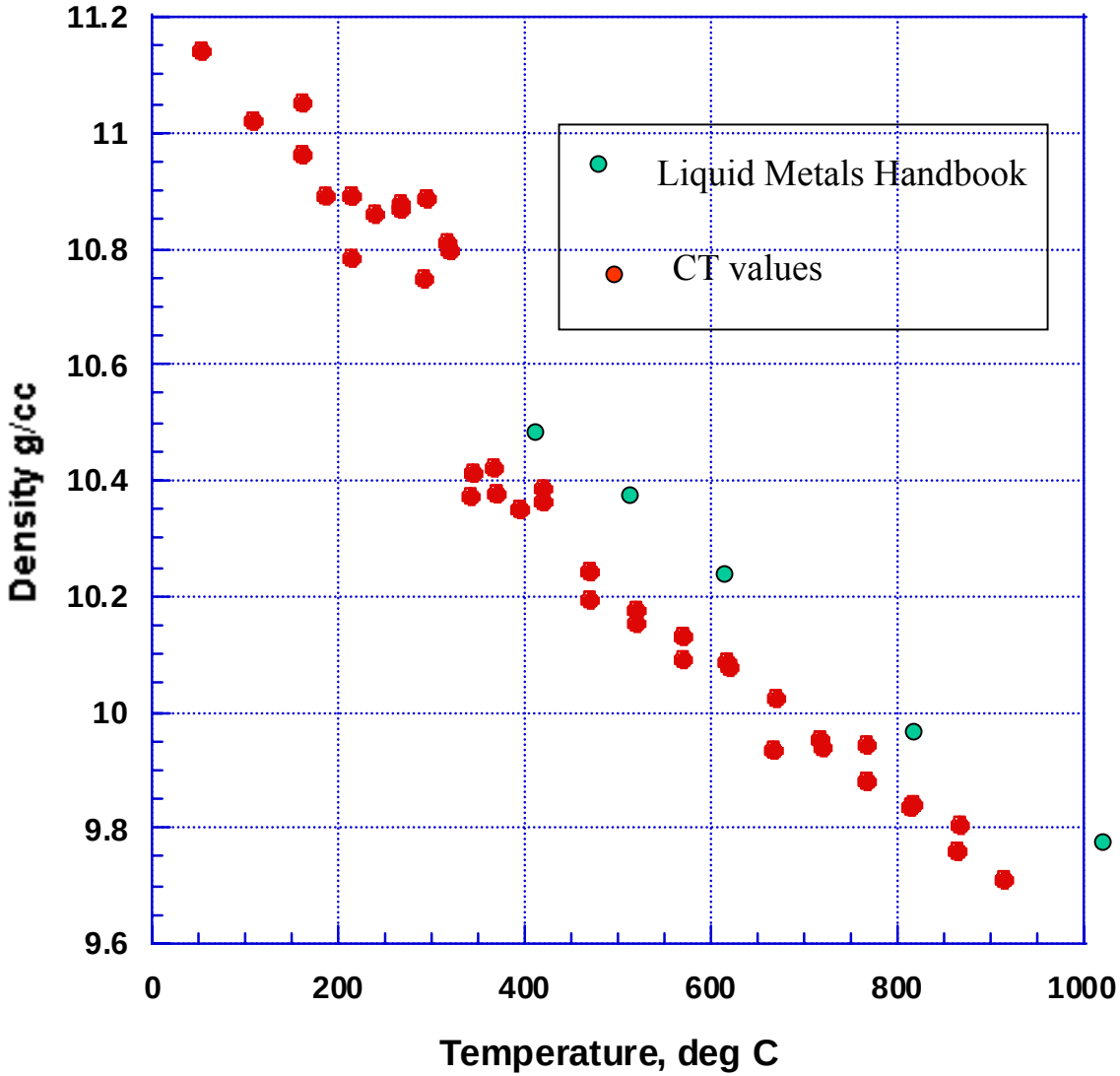
Digital radiograph showing lead sample and heat pipe within furnace.

CT section through furnace

Showing standards, furnace windings (f), heat pipe (h), fused silica tube (s), and Pb sample (P)

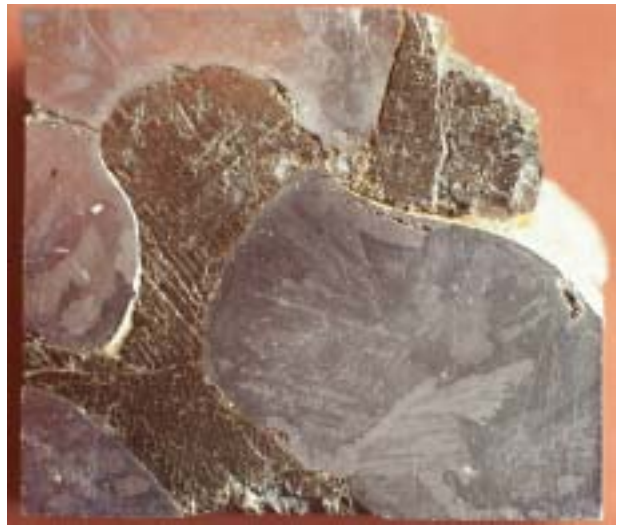


CT Measurement of Density of Lead



Mundrabilla meteorite

an example of space grown material



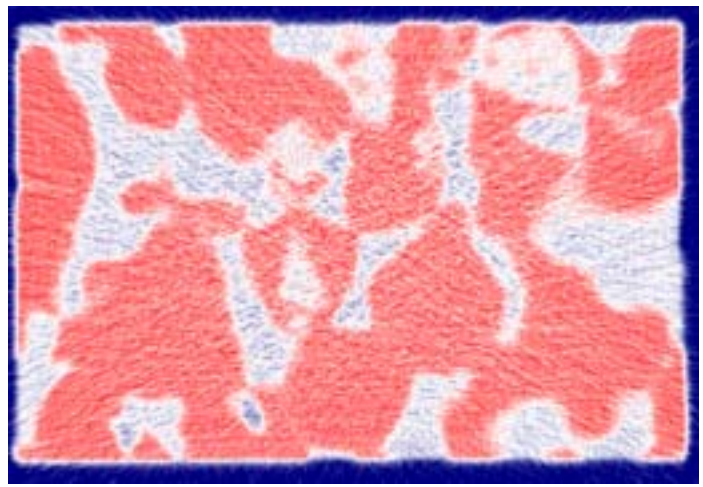
Unique structure of 75vol% metal and 25vol% iron sulfide

Formation mechanism – unknown, mysterious

Coarsened dendritic structure, slowly cooled after solidification.

CT uniquely suited to examine internal structure

2’4” long, 100 lbs weight

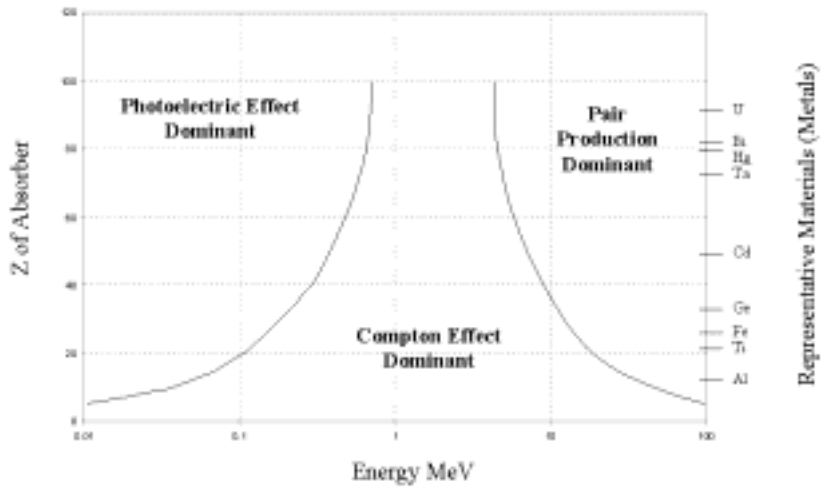


CT slice, one of 150 taken so far

Conclusions

Technique is invaluable as a non-destructive analysis tool
Useful for measuring thermal expansion
future planned Pb-Sb alloy, Al-Cu alloy, CdTe, InSb, Ge, Ge-Si, HgCdTe, Te, others
Internal structure of Mundrabilla meteorite
Patiently awaiting ISS processed samples

Some fundamental scattering theory



$\mu_C \sim K\ {}_2Z/f(E)$ for Compton scattering

Compton Effect dominant in range of ^{60}Co isotope (1.17 and 1.33 MeV)

For an incident beam of intensity I_0, the transmitted intensity is I as deduced from the following equation:

$$I = I_0 \exp(-\mu s), \qquad (1)$$

where μ is the linear attenuation coefficient for the material and s is the thickness of the absorber. For multiple absorbers with different elements the attenuation effect is linearly additive so that

$$I = I_0 \exp-(m_1 s_1 + m_2 s_2 + \ldots m_n s_n), \qquad (2)$$

where μ_n is the linear absorption coefficient of the nth element in the path and s_n is its thickness.
In two dimensions, the position of the nth element can described by coordinates x and y such that equation 2 becomes:

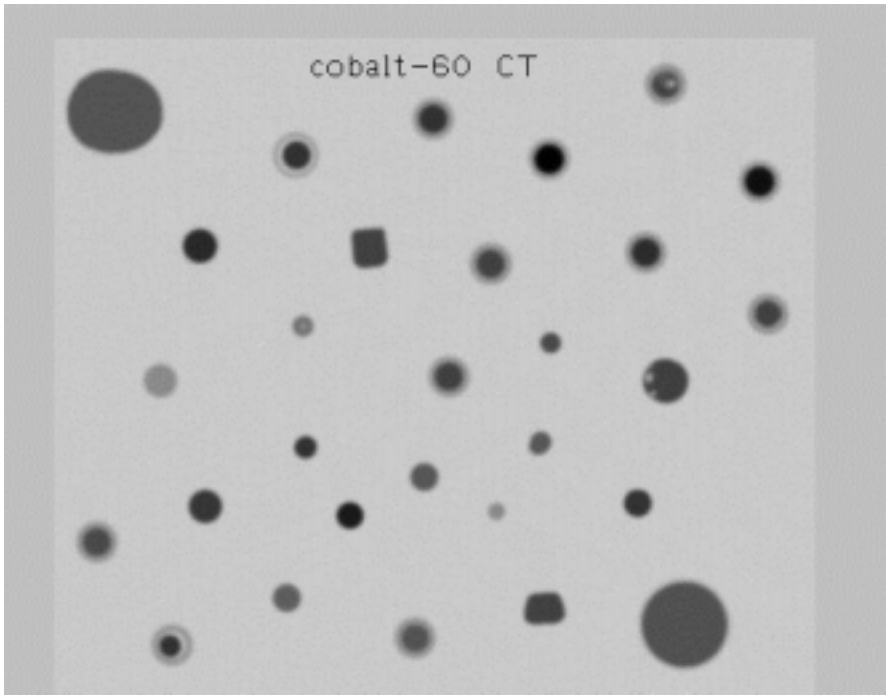
$$I = I_0 \exp - [\int_{source}^{detector} m(x,y)ds] \qquad (3)$$

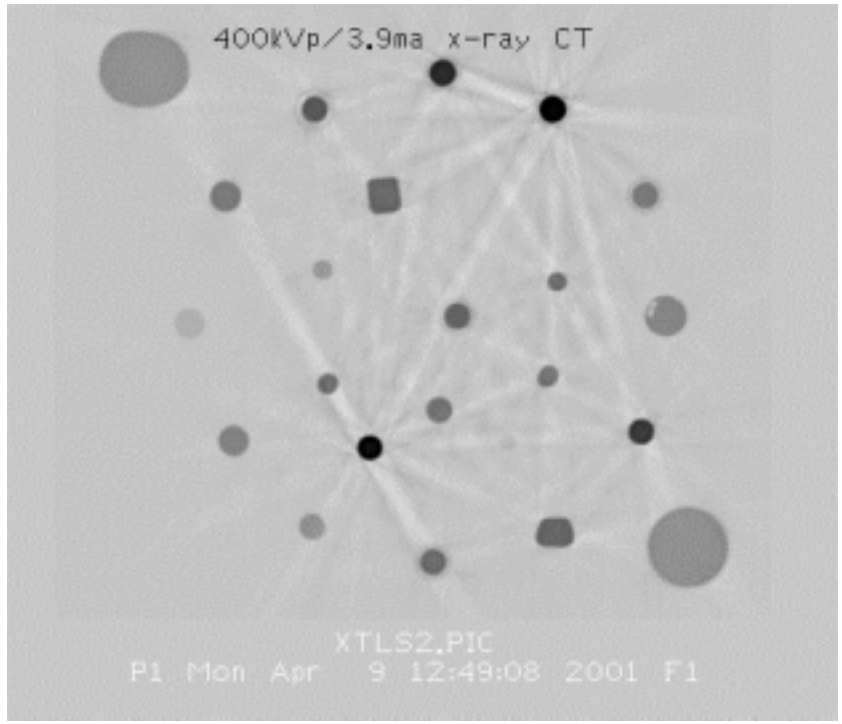
By dividing by I_0 and taking logs, equation 3 becomes the Radon transformation of m(x,y), a fundamental equation of the CT process:

$$P = \ln(I_0/I) = [\int_{source}^{detector} m(x,y)ds] \qquad (4)$$

Why we use ^{60}Co

Computed Tomography -Sections through standards



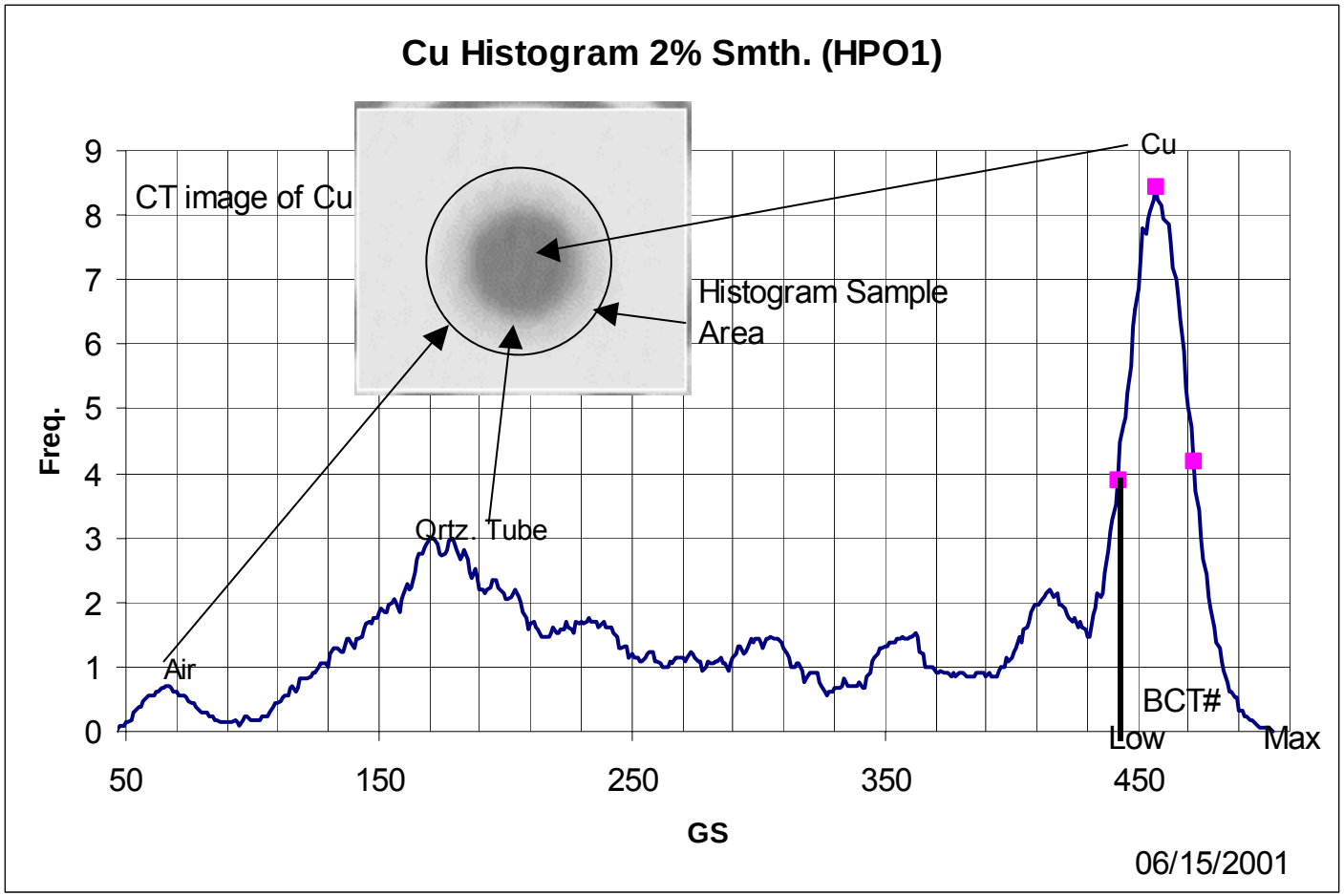


^{60}Co radioisotope

(1.17 and 1.33 MeV)

X-Ray (Bremsstrahlung)

Continuous energy spectrum

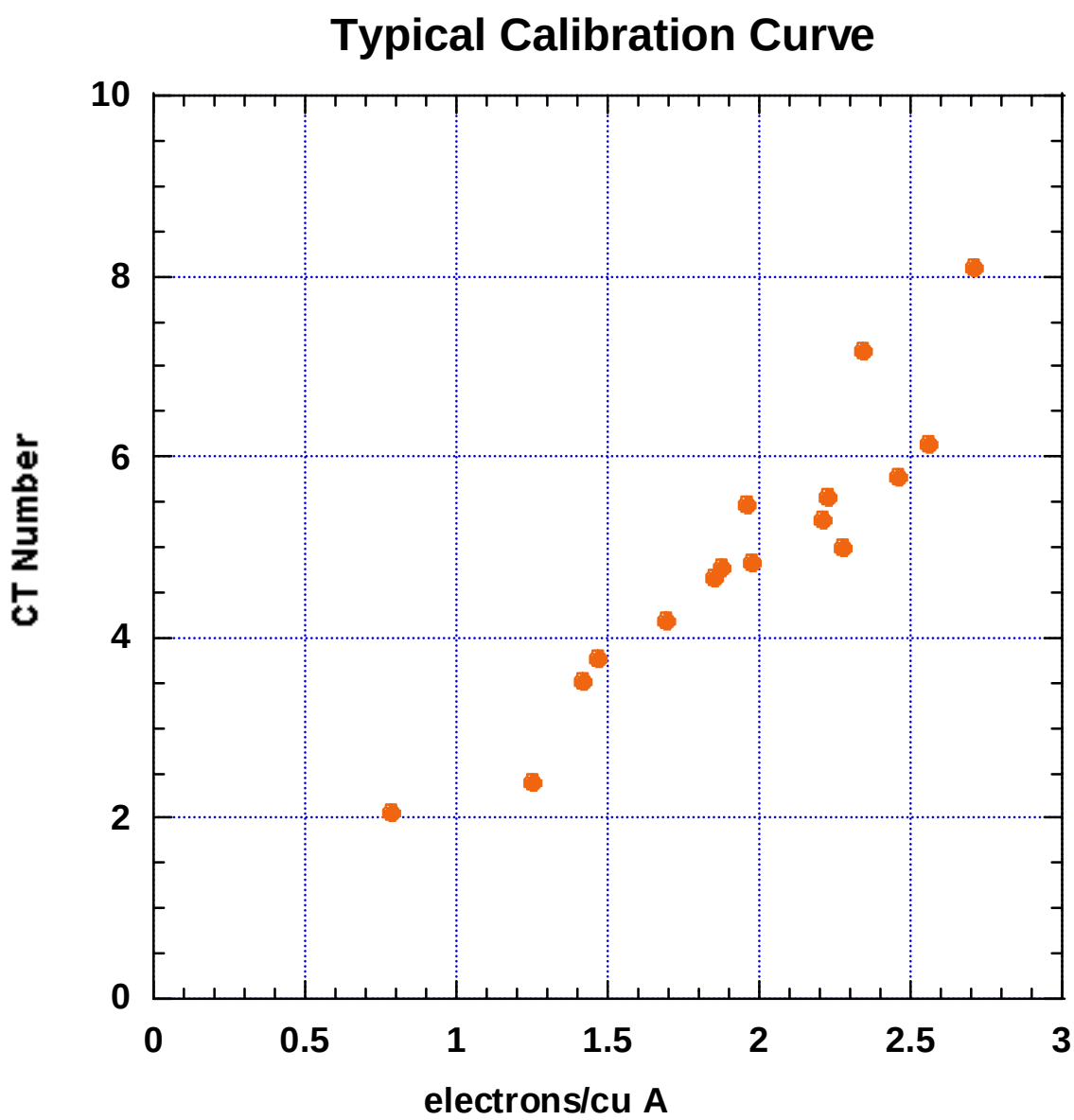


Histogram of Cu standard within a fused silica tube

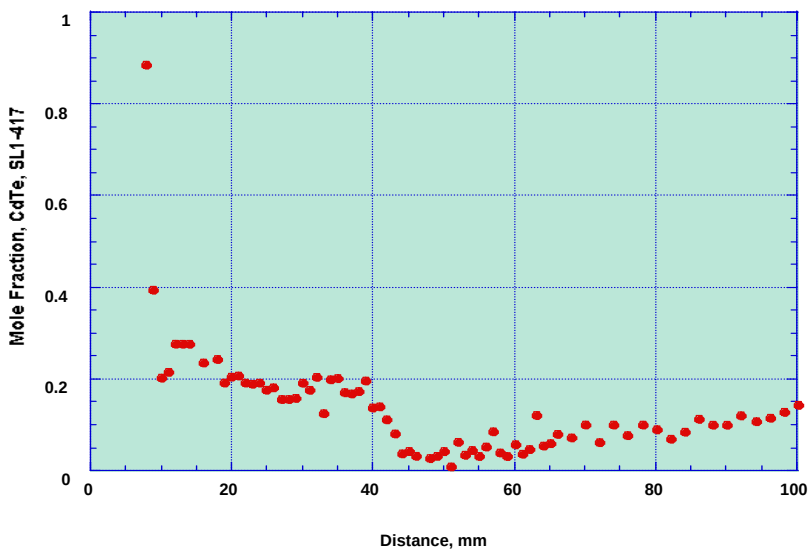
Plot of CT number against calculated electron density for a set of standards (elements and stoichiometric compounds).

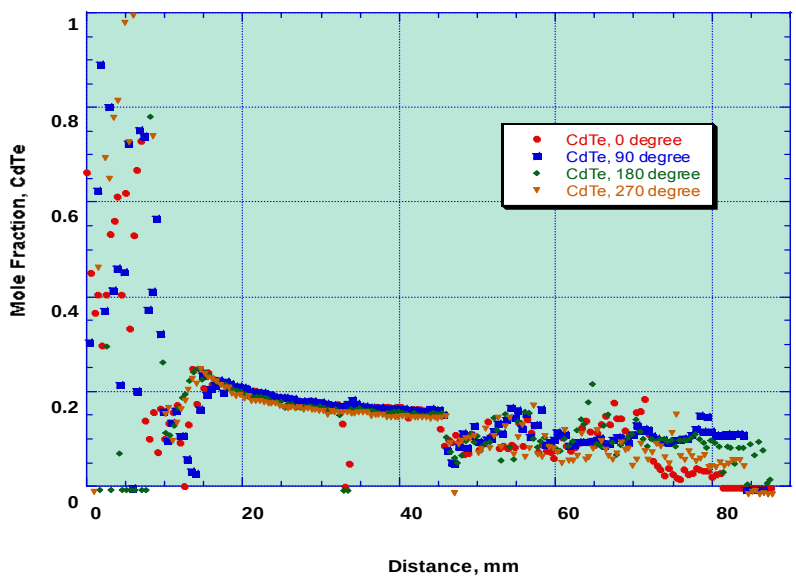
Density calculated from the linear absorption coefficient, μ, divided by the mass absorption coefficient, μ/ρ.

CT number is the measured attenuation and is proportional to the linear absorption coefficient. In the Compton range, the MACs are almost, but not quite constant, for all elements.



Ground Truth Analysis of HgCdTe Boule for USMP-4 Flight Experiment



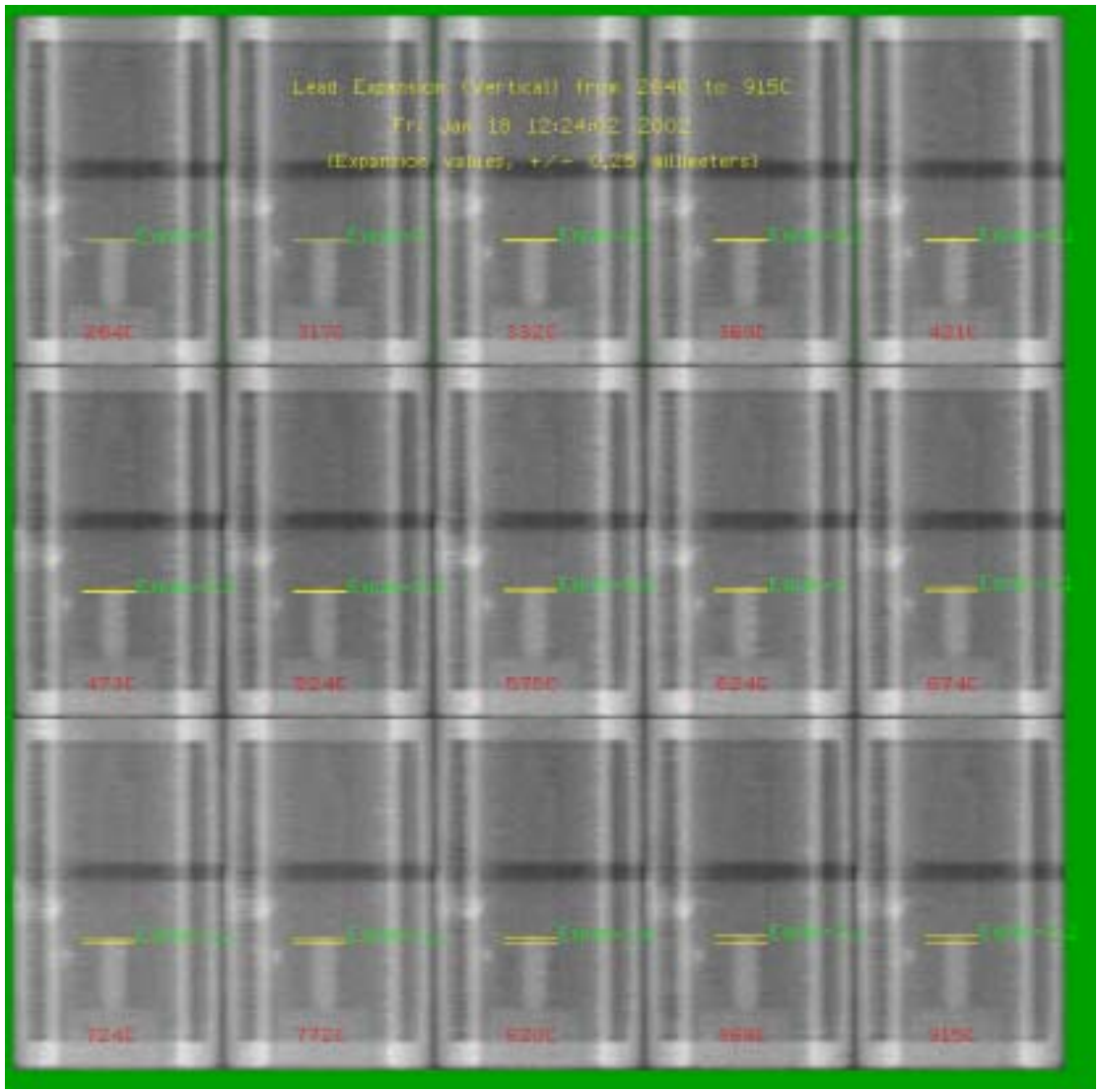


CT determination of Composition

Wavelength Dispersive Spectrometry of four surfaces

Note how the CT averages the composition compared to the spread of the WDS Data. The WDS data is influenced by surface anomalies (e.g. pure Hg)

Digital Radiographs showing thermal expansion of Lead



An Overview of Materials Science Research at the MSFC Electrostatic Levitator Facility and Recent CDDF Efforts

J.R. Rogers[1], R.W. Hyers[1], T. J. Rathz[2], M.B. Robinson[1] and K.F. Kelton[3]

[1]*NASA Marshall Space Flight Center, SD46*

[2]*University of Alabama in Huntsville*

[3]*Washington University in St. Louis*

Contact: *jan.rogers@msfc.nasa.gov, 256-544-1081.*

Abstract

Containerless processing is an important tool for materials research. The freedom from a crucible allows processing of liquid materials in a metastable undercooled state, as well as allowing processing of high temperature and highly reactive melts. Electrostatic levitation (ESL) is a containerless method which provides a number of unique advantages, including the ability to process non-conducting materials, the ability to operate in ultra-high vacuum or at moderate gas pressure (~5 atm), and the decoupling of positioning force from sample heating. ESL also has the potential to reduce internal flow velocities below those possible with electromagnetic, acoustic, or aero-acoustic techniques. In electrostatic levitation, the acceleration of gravity (or residual acceleration in reduced gravity) is opposed by the action of an applied electric field on a charged sample. Microgravity allows electrostatic levitation to work even more effectively. The ESL facility at NASA's Marshall Space Flight Center (MSFC) is in use for materials research and thermophysical property measurement by a number of different internal and external investigators. Results from the recent CDDF studies on the high energy X-ray beamline at the Advanced Photon Source of Argonne National Laboratory will be presented. The Microgravity Research Program supports the facility.

An Overview of the MSFC ESL Facility and the CDDF Beamline Studies

Dr. Jan Rogers, SD46

ESL Facility Scientist

Agenda

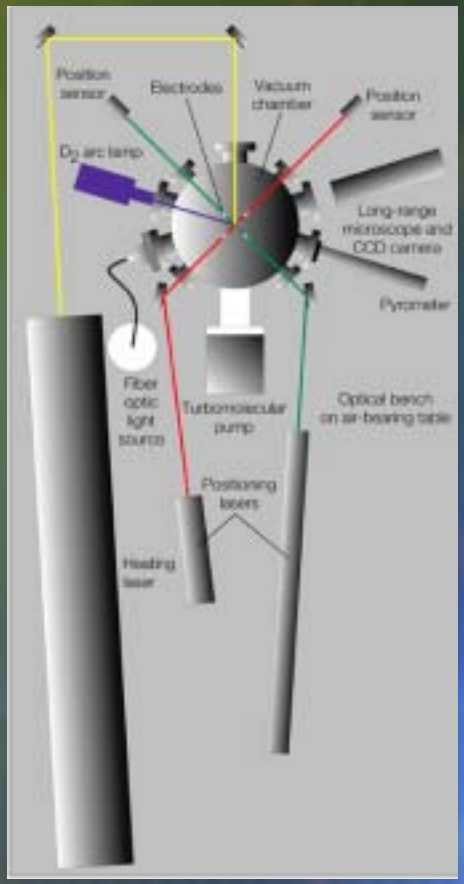
- Introduction
- ESL system and processing
- Scientific Investigations
- Results
- Future work- ESL Facility
- CDDF Beamline ESL studies
- Future work-BESL

ESL Team

- Science Team
  - Trudy Allen, ICRC
  - Glenn Fountain, Morgan Research
  - Ken Haynes, CSC
  - Doug Huie, ERC
  - Dr. Robert W. Hyers, SD46
  - Tom Rathz, UAH
  - Dr. Michael B. Robinson, SD46
  - Dr. Jan R. Rogers, SD46
  - Kevin Vellacott-Ford, SD22
- Programmatic Team
  - Pat Doty, SD44
  - Dave Schultz, Pace and Waite

ESL

- Processes or melts levitated samples
- Provides a quiescent environment for the samples
- Is an important containerless technique for the study of metals, alloys, glasses, ceramics and semiconductors
- Is a ground-based technique which could be performed in microgravity



J.R. Rogers, MSFC

ESL Processing

- ESL data is pushing the envelope of materials science for high temperature and undercooled materials
- High temperature materials are accessible for study
  - –Interaction with a container is not a concern
  - –Applications include characterization and development of materials for advanced propulsion
  - –Materials for Advanced Propulsion is a special theme for the current Code U NRA
  - –MSFC and external proposals for use of ESL anticipated for current Code U NRA

J.R. Rogers, MSFC

ESL Processing

- Deep undercooling possible (no container-induced nucleation)
  - –Containerless data has led to novel advanced materials and products
  - –Bulk metallic glasses of Dr. Johnson (Caltech) resulted in
    - •Liquidmetal™ Golf clubs
    - •Solar wind collectors for NASA's Genesis Spacecraft, launched 8/8/01
    - •Other possible applications for DOD

J.R. Rogers, MSFC

ESL Capabilities

- Undercooling and metastable state formation
- Study of very high-temperature materials
- Phase diagram determination
- Thermophysical properties
  - Surface tension
  - Viscosity
  - Heat capacity
  - Density

Thermophysical data are important for advanced modeling of welding and casting

J.R. Rogers, MSFC

ESL Investigators

Johnson Group

Kelton Group

Bayuzick

Day Group

ESL Investigators

Results

MSFC improvements in ESL subsystems and operational protocols resulted in high output:

- **Data for more than 1,700 melt cycles delivered to customers in FY02 to date**
- **More than 1,400 melt cycles in FY01**
- **More than 3,100 melt cycles in FY00**
- **Improvements include UV charging system, position detection and control apparatus and code**
- **One patent application filed and three invention disclosures pending**
- **Numerous publications and presentations for PI community**
- **Support for milestone reviews**

Future Work

- Support Science Concept Reviews
  - Dr. Kelton, Washington University in St. Louis (PI visit in 8/02)
  - Dr. Flemings, MIT (PI visit to ESL 6/02)
- Additional near-term PI visits:
  - Dr. Bayuzick, Vanderbilt University
  - Dr. Day, University of MO, Rolla

Future Work

- New chamber under procurement to
  - –process samples at vacuum and pressures up to 5 atmospheres
  - –permit control of gaseous environment around sample
    - •Controlled partial pressure of O_2 desired for oxides
    - •Reducing environment such as He/ 4% H_2 desired for some alloys
  - –improve processing capabilities for ceramics, glasses, and high–vapor pressure materials
    - •Vapor deposition/outgassing rates reduced-resulting in increased throughput
- Final mechanical design review completed 3/02
- Software review anticipated 6/02
- Delivery and installation of system anticipated summer of ‘02

CDDF: In Situ Observations of Structural Transformations in Undercooled Liquids via BESL

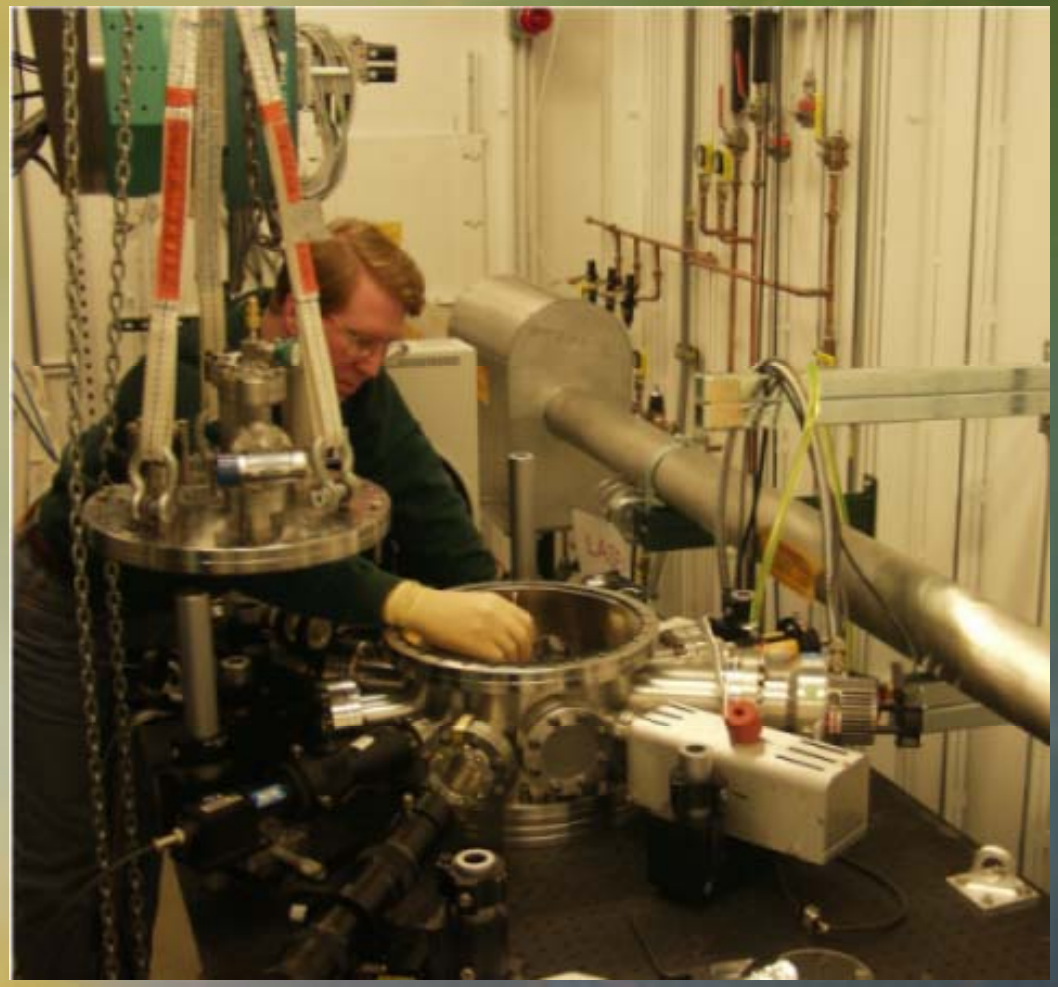
- **MSFC team:** Dr. Jan Rogers, PI, SD46; Dr. R.W. Hyers, SD46; Dr. M.B. Robinson, SD46; Mr. T.J. Rathz, UAH; Mr. G. Fountain, Morgan Research; and Mr. D. Huie, ERC

- **Washington University in St. Louis team:** Dr. K.F. Kelton, Dr. A. Gangophadhyay and G. W. Lee

- **Goal:** To develop and utilize a new materials science research tool to meet NASA needs for materials development and characterization

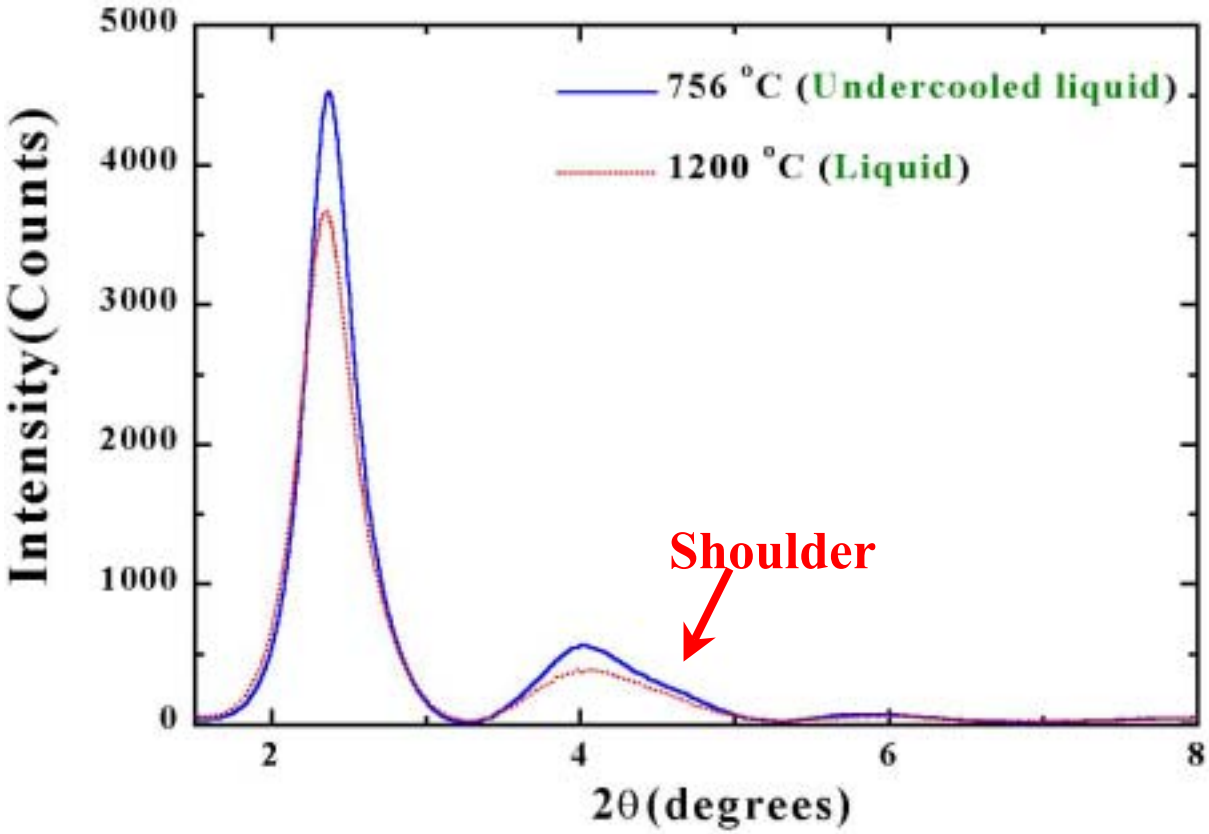
- **Status:** MSFC BESL proof-of-concept unit developed and tested at the high energy beamline at the Advanced Photon Source of Argonne National Laboratory.

BESL on 125 KEV beamline at Argonne National Labs



Preliminary Data from BESL

Liquid data corrected for background



- *Shoulder of 2nd peak suggests increased icosahedral ordering*
- *In agreement with modeling prediction*

BESL X-ray image

Inconel during melting ~ 1327 C

BESL Results

- **Results:** More than 500 melt cycles for alloys including: TiZrNi (quasicrystal-forming alloy), Ni, Hastelloy and Inconel

- **BESL advances to the state-of-the art:** Reduced internal flow velocities and thermal gradients in BESL compared to EML or aerodynamic methods. BESL data are superior and show structural transformations during quasicrystal formation.

- **Benefit to MSFC:**
  - –Provides data for OBPR Materials Science Research Program
  - –Proof-of-concept study demonstrated that method can be used for phase diagram determination of high-temperature materials.

- **Motivation for in-house effort:** MSFC ESL facility is a world-leader in ESL technology. BESL supports Microgravity projects and may contribute to advanced propulsion materials needs.

BESL Future Work

- Complete data analysis from FY02 efforts
- Prepare and submit journal articles
- Seek funding to upgrade proof-of concept unit to make a BESL unit optimized for high-temperature materials research on the beamline. Sources include Code U NRA.
- Conclude CDDF efforts with FY03 visit to Argonne and analysis

The Role of Convection and Growth Competition on Phase Selection in Microgravity (LODESTARS)

PI: Prof. Merton C. Flemings, MIT
Co-I: Prof. Douglas M. Matson, Tufts University
Co-I: Dr. Jan R. Rogers, NASA MSFC SD46
Co-I: Dr. Robert W. Hyers, NASA MSFC SD46

For a wide range of compositions, Fe-Cr-Ni alloys can solidify by a two-step process: a metastable solid forms first, subsequently transforming into the stable solid phase. This two-step solidification produces a profoundly different microstructure, and therefore different properties, in the final solid.

The delay time between the two steps of the solidification process varies from microseconds to seconds. This delay time is a strong function of composition and a weak function of the undercooling of the melt below the metastable liquidus. From the results obtained during the MSL-1 mission and in ground based electrostatic levitation testing at NASA MSFC, we also know that convection also has a significant effect on the delay time. By examining the effect of convection on delay time over a wide range of convection, for several different alloys, we can gain a better understanding and better control of the microstructural evolution and final structure of stainless steel alloys.

MSFC provides ESL for ground-based testing in a low-convection state, and the numerical modeling that enables estimation of the convection levels under the different process conditions.

The Role of Convection and Growth Competition in Phase Selection in Microgravity (LODESTARS)

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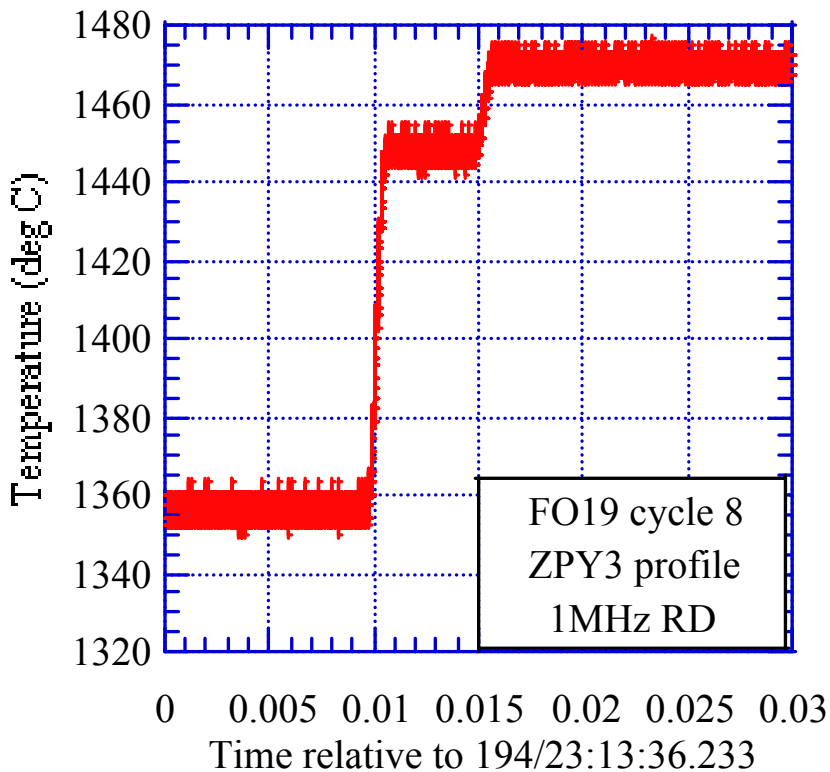
LODESTARS:
Phase Selection and Double Recalescence

Two-step solidification

- Metastable ferrite (FCC) phase forms first.
- Transformation to stable austenite (BCC) phase.
- Delay of µs to sec.

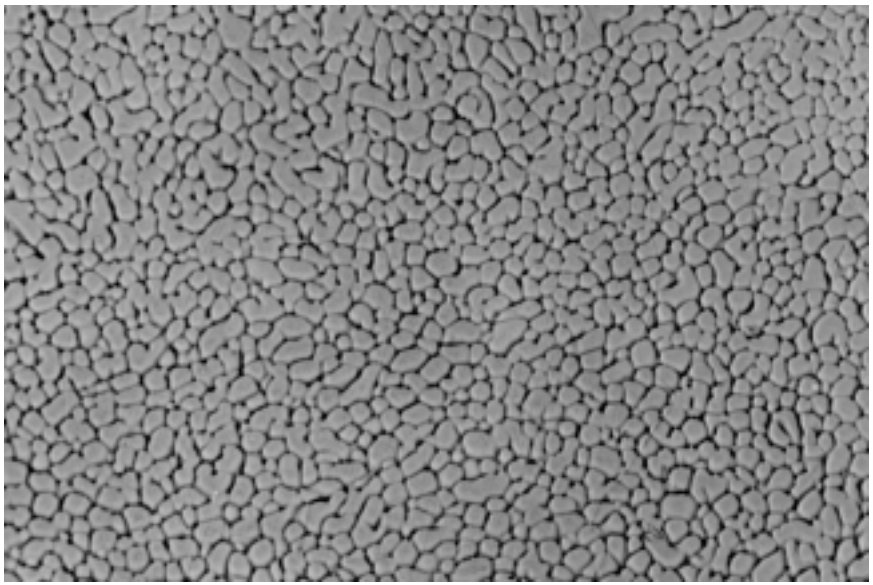
Delay time depends on

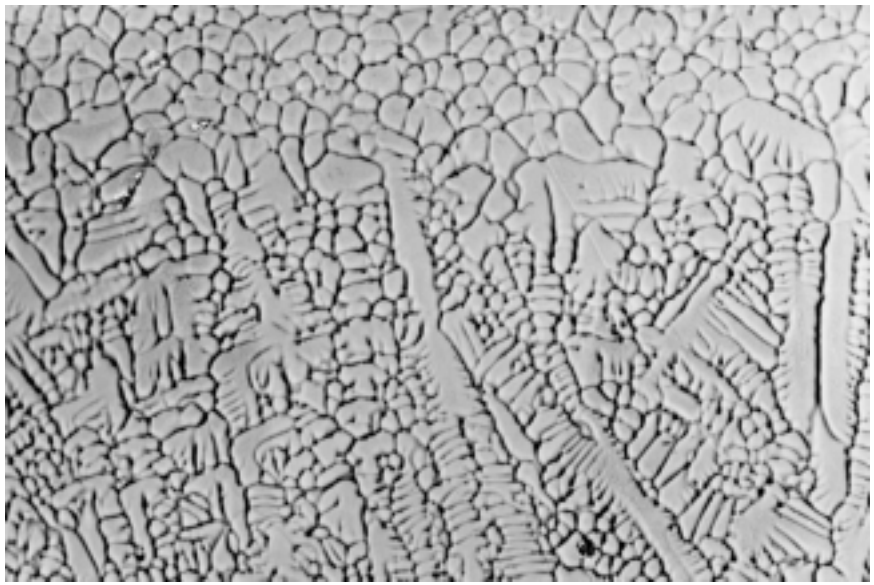
- Composition
- Initial Undercooling
- Convection: observed on MSL-1



M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

Double vs. Single Recalescence





200 µm

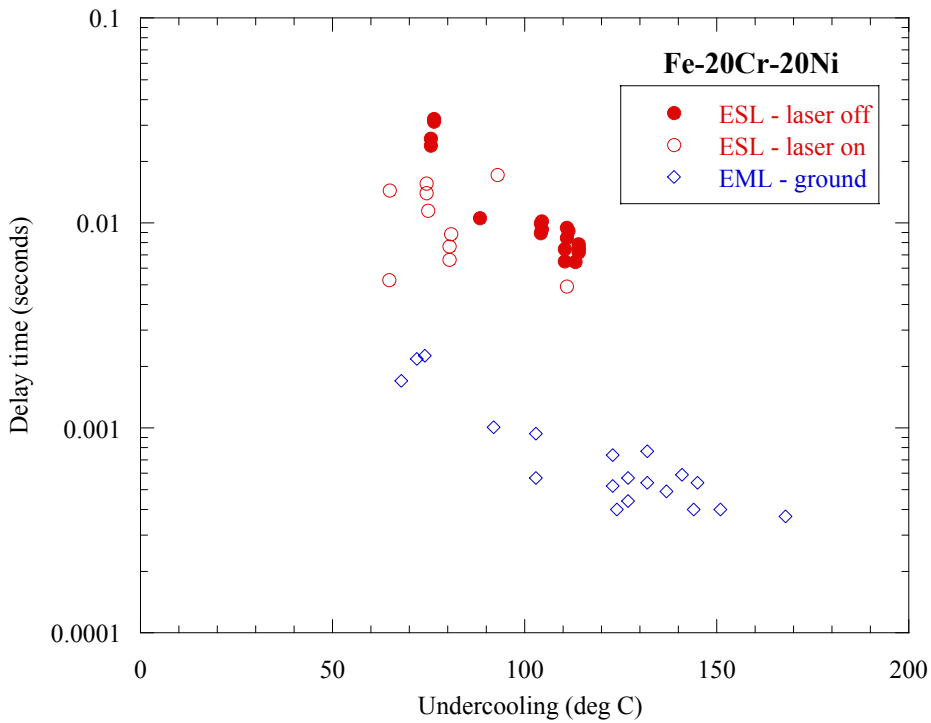
Double Recalescence

Single Recalescence

M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

Importance of Convection

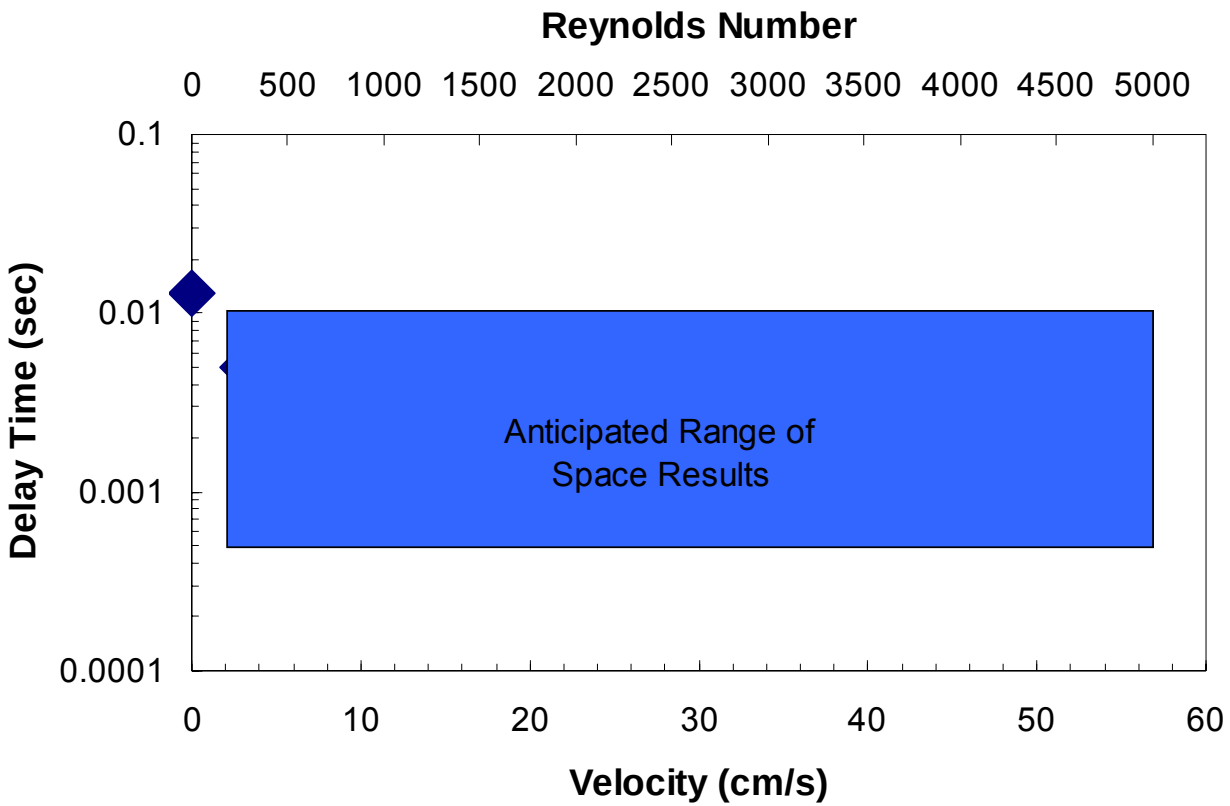
- One sample
- Three levels of convection:
  - ESL laser off ~ 0 cm/s
  - ESL laser on ~ 6 cm/s
  - EML ~ 50 cm/s
- Fluid flow decreases delay time ~ 10X.



M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

Understanding the Effect of Convection on Delay Time

Fe-20Cr-20Ni Alloy, 100 K undercooling



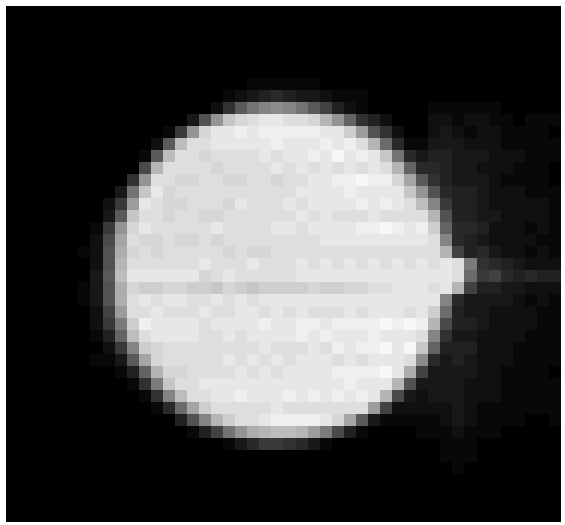
M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

LODESTARS at MSFC

- MSFC Co-Investigators:
  - Jan Rogers, SD46
  - Robert Hyers, SD46
- MSFC Contributions:
  - Experiments at Electrostatic Levitator.
  - Metallography and analysis.
  - Modeling of convection.

LODESTARS in ESL

- Double Recalescence in 72Fe-11.2Cr-16.8Ni Stainless Steel.
- Processed in MSFC ESL July 23, 2001.
- Recorded at 40,500 frames/sec, played at 10 frames/sec.
- Undercooled liquid is gray, primary (metastable) ferrite is red, and secondary (stable) austenite is yellow.



M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

Importance of Modeling

Computational methods are the only means to assess convection in this system:

- Opaque, featureless sample:
  - No laser Doppler velocimetry.
- High temperature, highly reactive sample, large magnetic field (in EML):
  - No Vives probe.
- Surface particles swept into stagnation lines:
  - No particle tracking velocimetry.

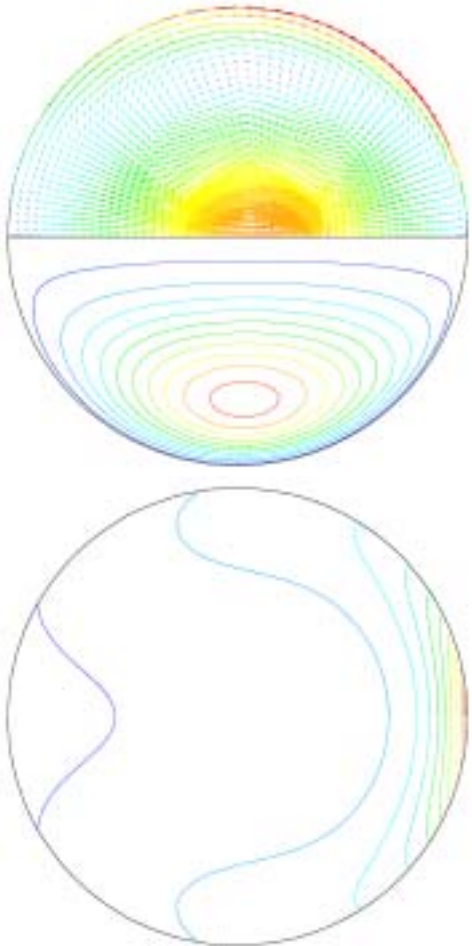
M.C. Flemings (MIT), D. Matson (Tufts), L. Kensel (MIT), R.W. Hyers (MSFC), and J.R. Rogers (MSFC)

Marangoni Convection in ESL FeCrNi

No rotation

FeCrNi drop at Tm

Maximum velocity = 13 cm/s

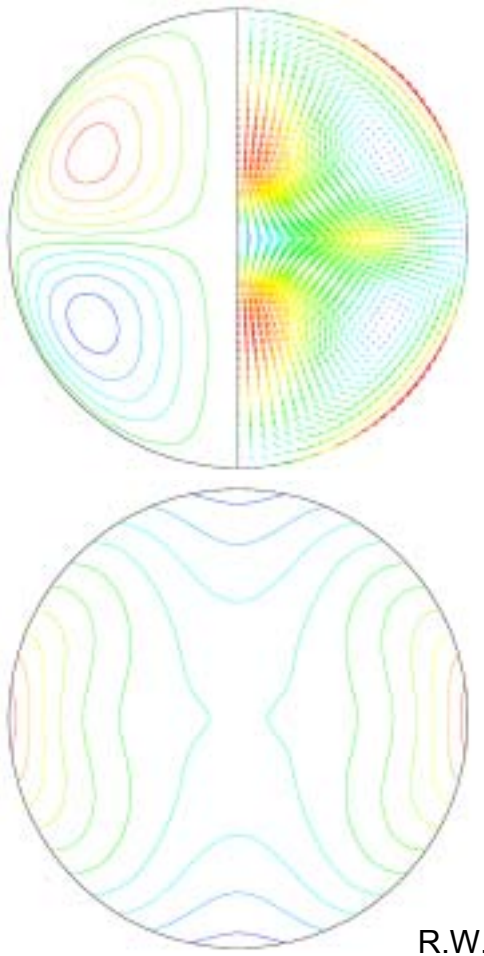


ΔT=29 K

Fast Rotation

FeCrNi drop at Tm

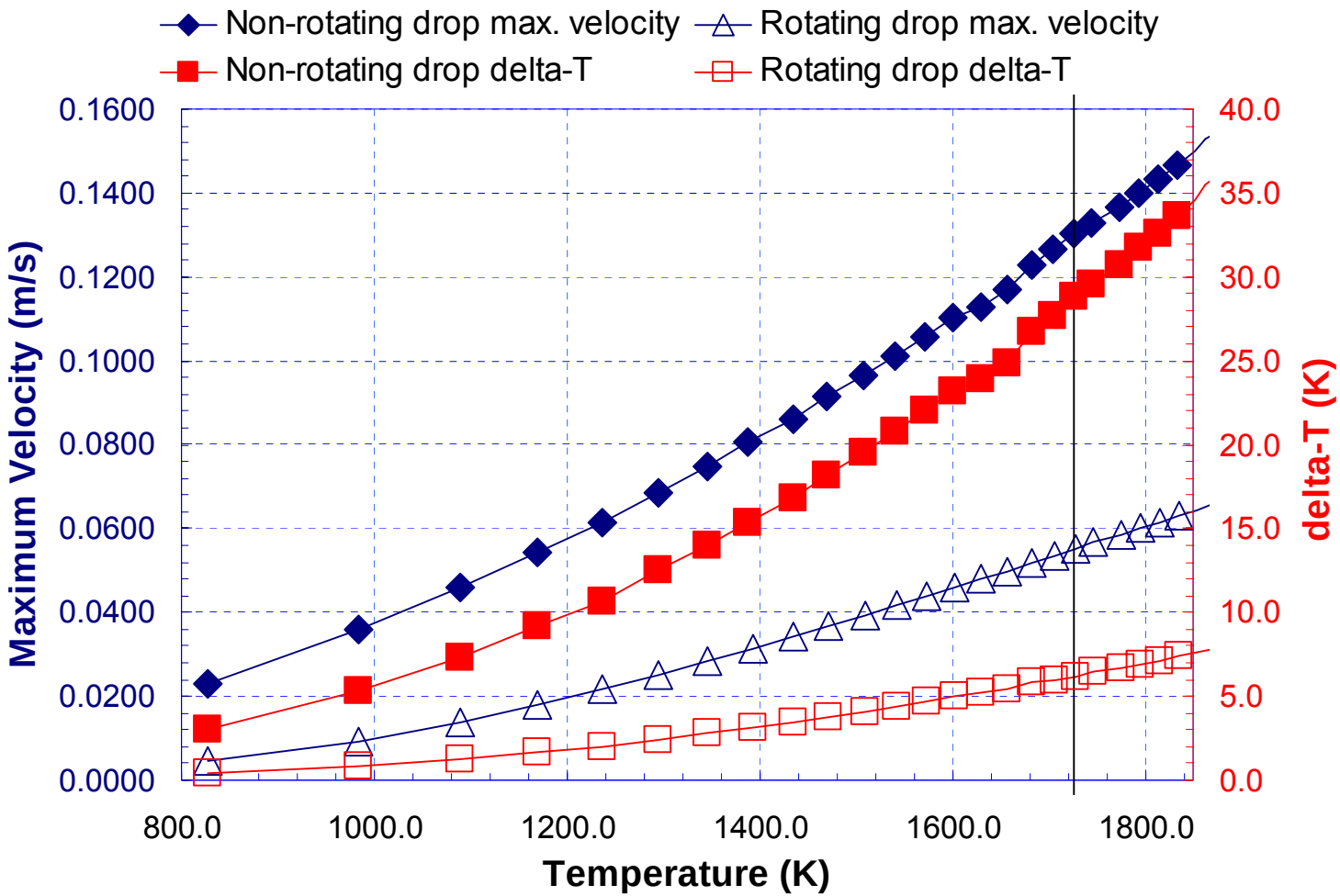
Maximum velocity = 5.6 cm/s



ΔT=6 K

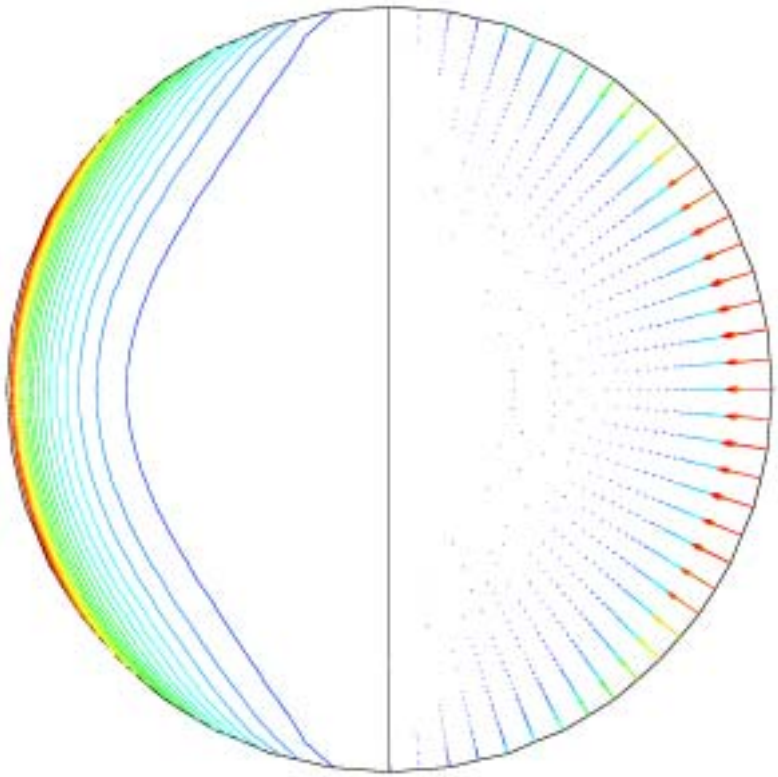
R.W. Hyers, NASA MSFC

Marangoni Convection in ESL

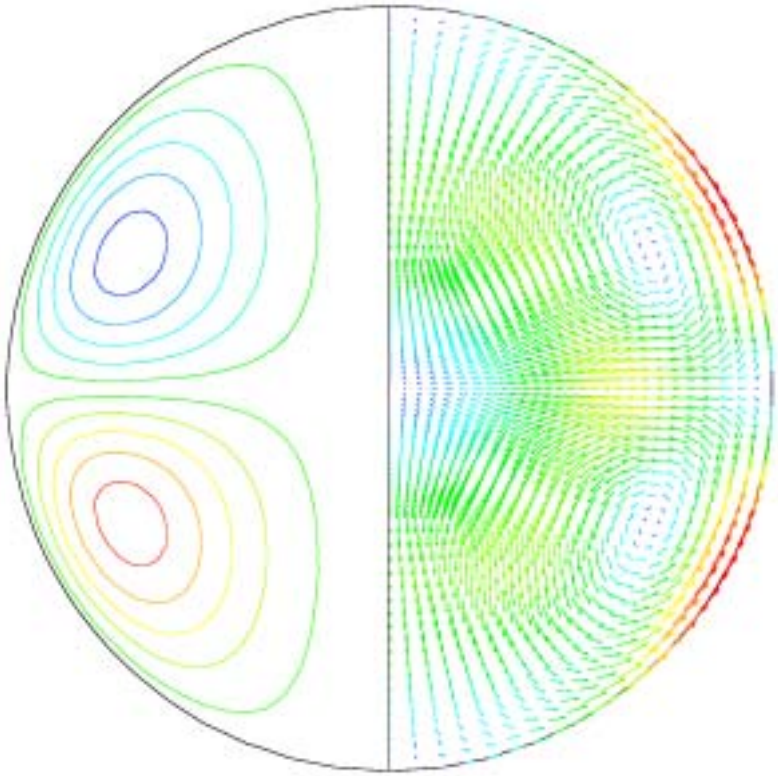


R.W. Hyers, NASA MSFC

EM Force and Flow



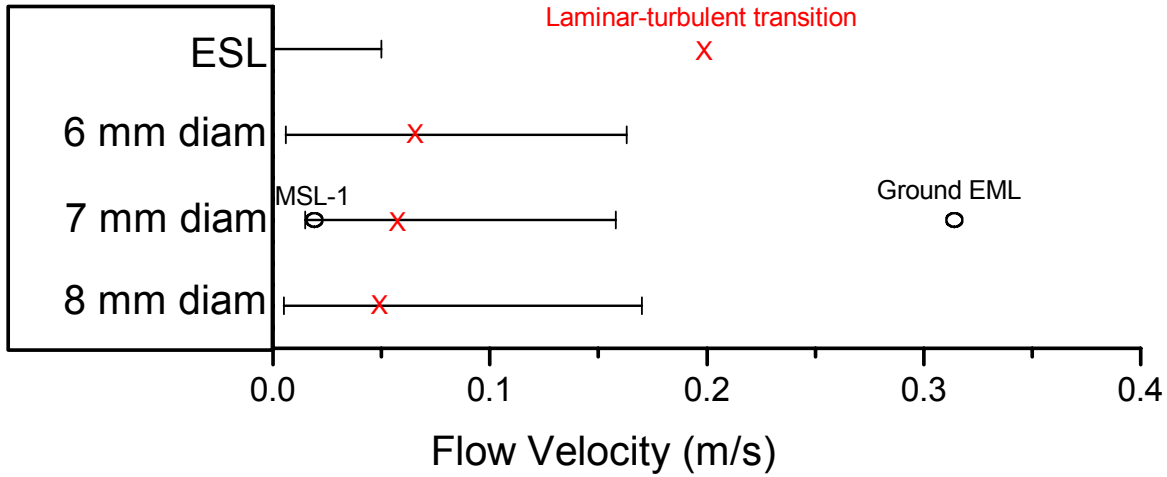
Electromagnetic force distribution for 150A positioning, 40.0A heating, TEMPUS MSL-1 coils, 7mm FeCrNi sample.

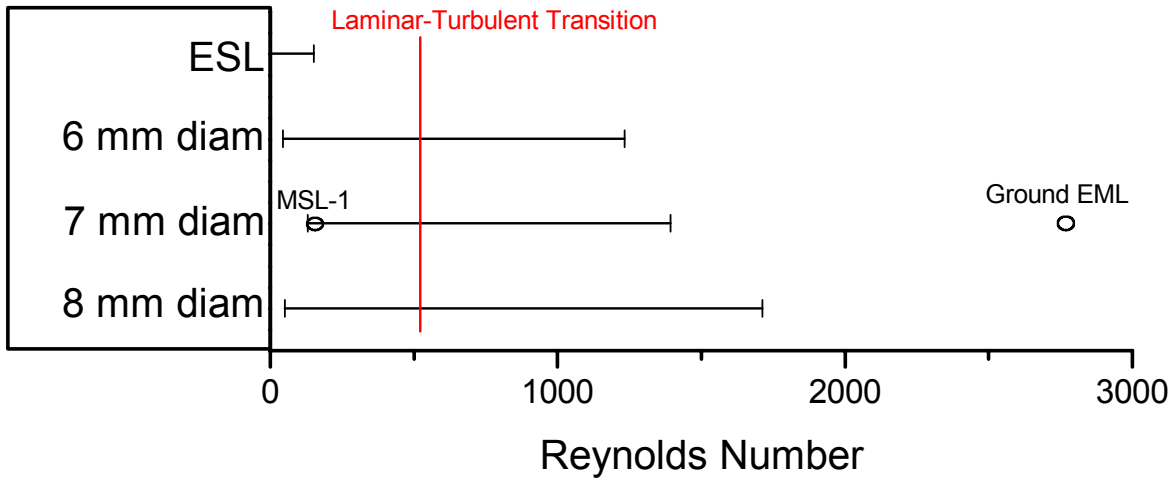


Flow for same conditions. Flow is heater dominated, inward at the equator, with 2 loops. Max velocity = 5.5 cm/s.

R.W. Hyers, NASA MSFC

Accessible Ranges for µg EML





Studies of Nucleation and Growth, Specific Heat and Viscosity of Undercooled Melts of Quasicrystals and Polytetrehedral-Phase-Forming Alloys (QUASI)

PI: Prof. Kenneth F. Kelton, Department of Physics, Washington University St. Louis
Co-I: Dr. Anup Gangopadhyay, Department of Physics, Washington University St. Louis
Co-I: Dr. Robert W. Hyers, NASA MSFC SD46

By investigating the properties of quasicrystals and quasicrystal-forming liquid alloys, we may determine the role of ordering of the liquid phase in the formation of quasicrystals, leading to a better fundamental understanding of both the quasicrystal and the liquid. A quasicrystal is solid characterized by a symmetric but non-periodic arrangement of atoms, usually in the form of an icosahedron (12 atoms, 20 triangular faces). It is theorized that the short-range order in liquids takes this same form. The degree of ordering depends on the temperature of the liquid, and affects many of the liquid's properties, including specific heat, viscosity, and electrical resistivity.

The MSFC role in this project includes solidification studies, phase diagram determination, and thermophysical property measurements on the liquid quasicrystal-forming alloys, all by electrostatic levitation (ESL). The viscosity of liquid quasicrystal-forming alloys is measured by the oscillating drop method, both in the stable and undercooled liquid state. The specific heat of solid, undercooled liquid, and stable liquid are measured by the radiative cooling rate of the droplets.

Studies of Nucleation and Growth, Specific Heat and Viscosity of Undercooled Melts of Quasicrystals and Polytetrehedral-Phase-Forming Alloys (QUASI)

- PI: Prof. Kenneth F. Kelton, Washington University St. Louis
- Co-I: Dr. Anup Gangopadhyay, Washington University St. Louis
- Co-I: Dr. Robert W. Hyers, NASA MSFC SD46

Quasicrystals

- Quasicrystals discovered in 1984.
- Symmetric but not periodic order.
- TiZrNi quasicrystals are icosahedral, 5-fold symmetric.
- Unique Electrical and Thermal properties:
  - **Thermal barrier coatings**
  - **IR Detector**
- Potential for Hydrogen Storage

K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

QUASI

- Theory: undercooled liquids show polytetrahedral ordering, as in quasicrystals.
- Change in liquid short range order should affect liquid properties:
  - **Heat capacity**
  - **Viscosity**
  - **Electrical resistivity**

K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

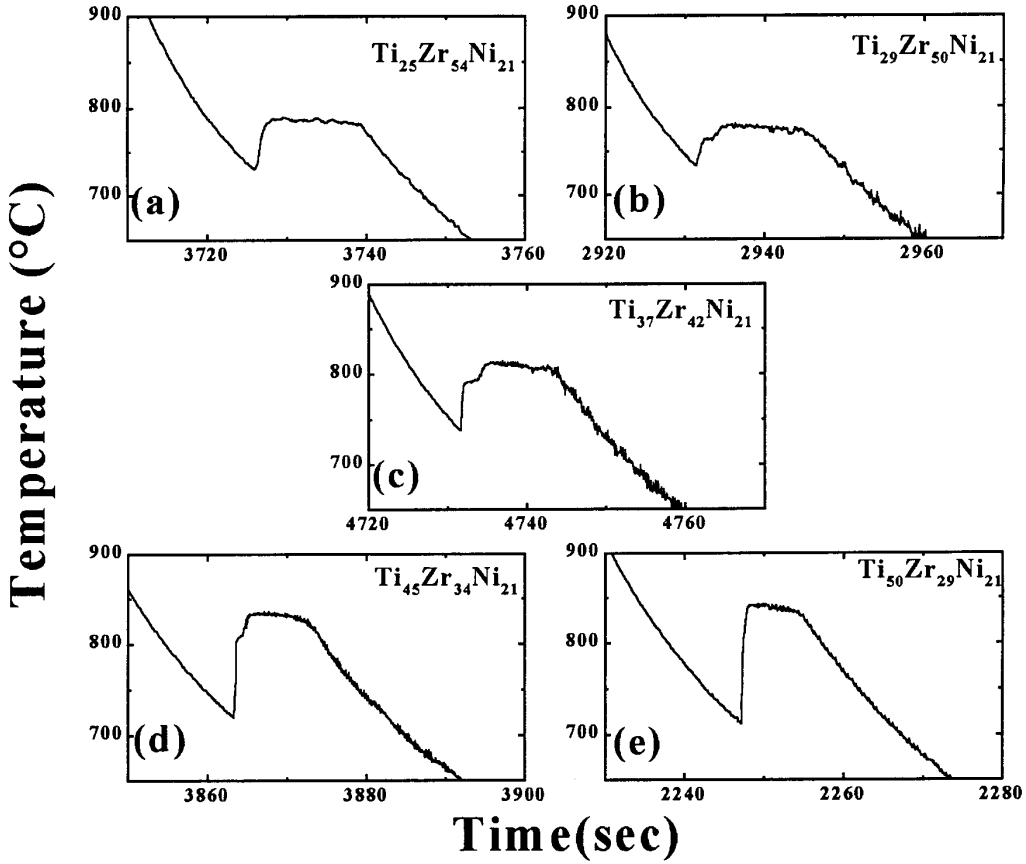
QUASI at MSFC

Electrostatic Levitation Experiments

- Phase Diagram and Solidification Path
- Thermophysical Property Measurement
  - **Viscosity, Specific Heat**
- Structure determination (BESL project)
- Modeling support for ESL and EML
  - **Can diffusion-controlled nucleation be achieved in ESL? In μg EML?**

K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

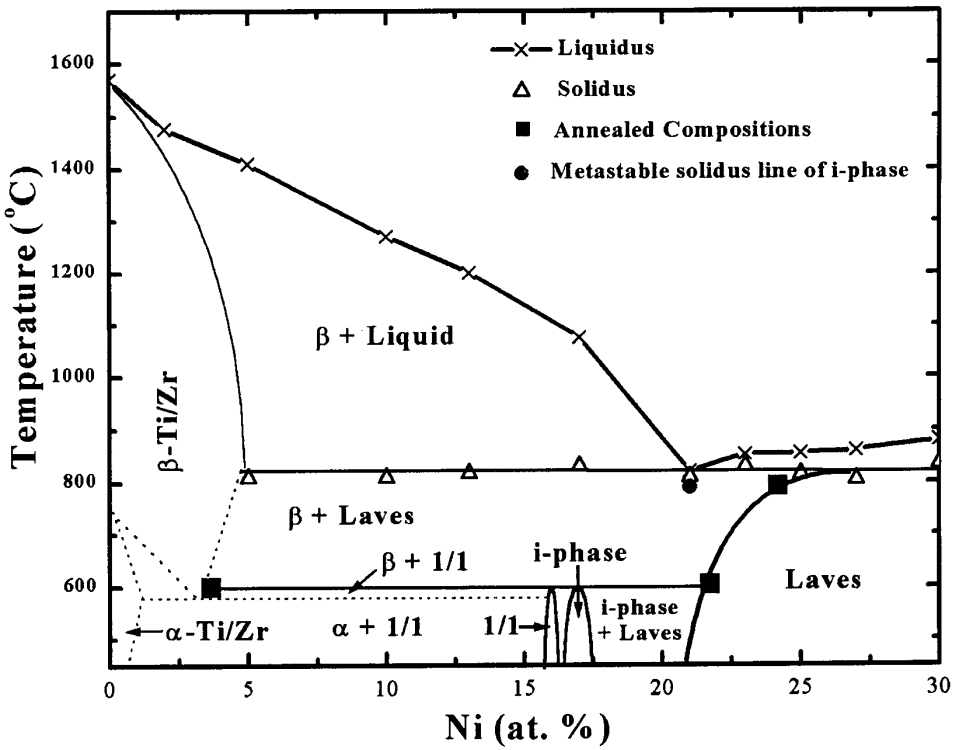
Solidification Path



K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

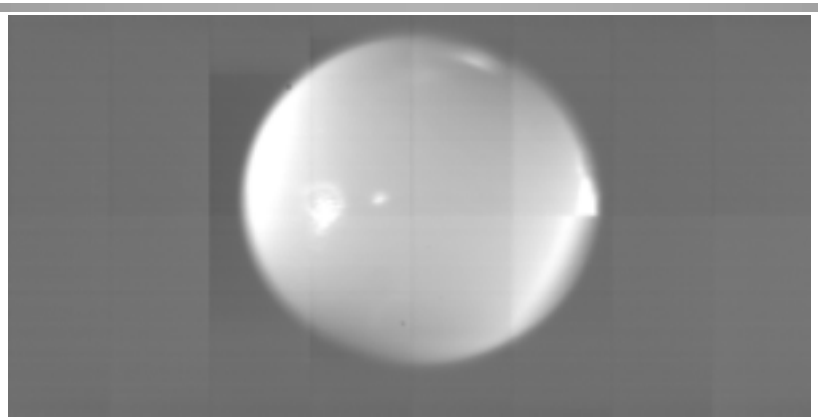
Phase Diagram

%Ti = %Zr



K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

Viscosity and Surface Tension



Damped oscillations in molten Zr at 1750ºC (T_m – 103 ºC) for measuring surface tension and viscosity in the MSFC ESL

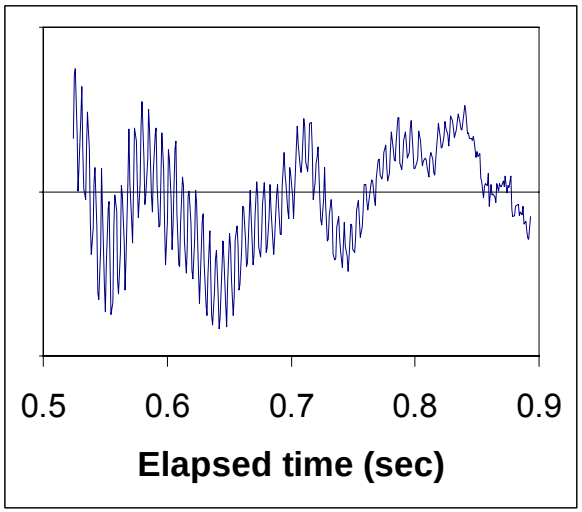
Recorded at 1000 frames/sec, played at 20 frames/sec

Oscillation frequency proportional to square root of surface tension (Rayleigh, 1879).

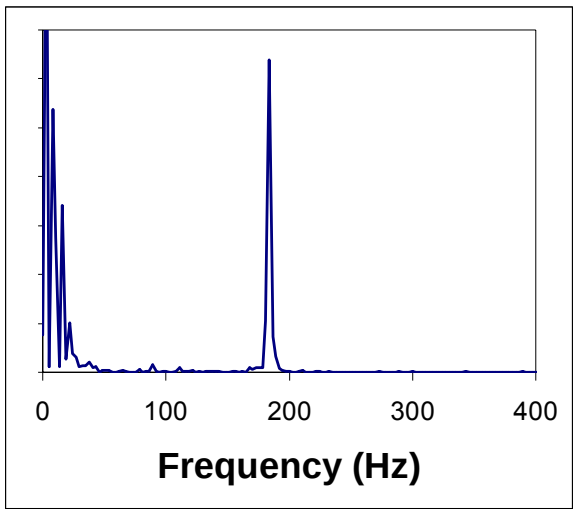
Damping time inversely proportional to viscosity (Lamb, 1881).

R.W. Hyers (NASA MSFC)

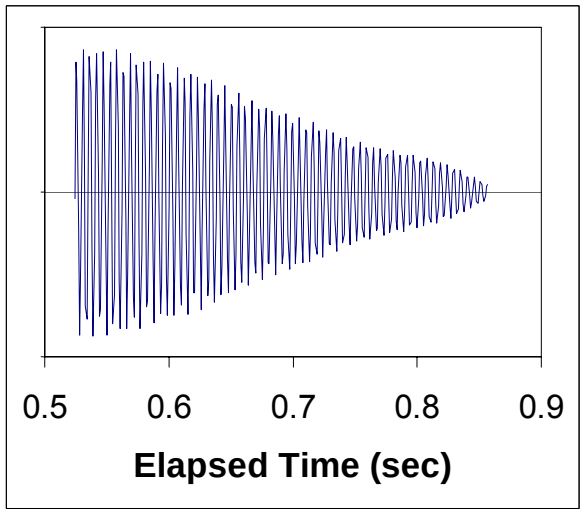
Measurement of Oscillations



Raw Area-Time Data



Power Spectrum

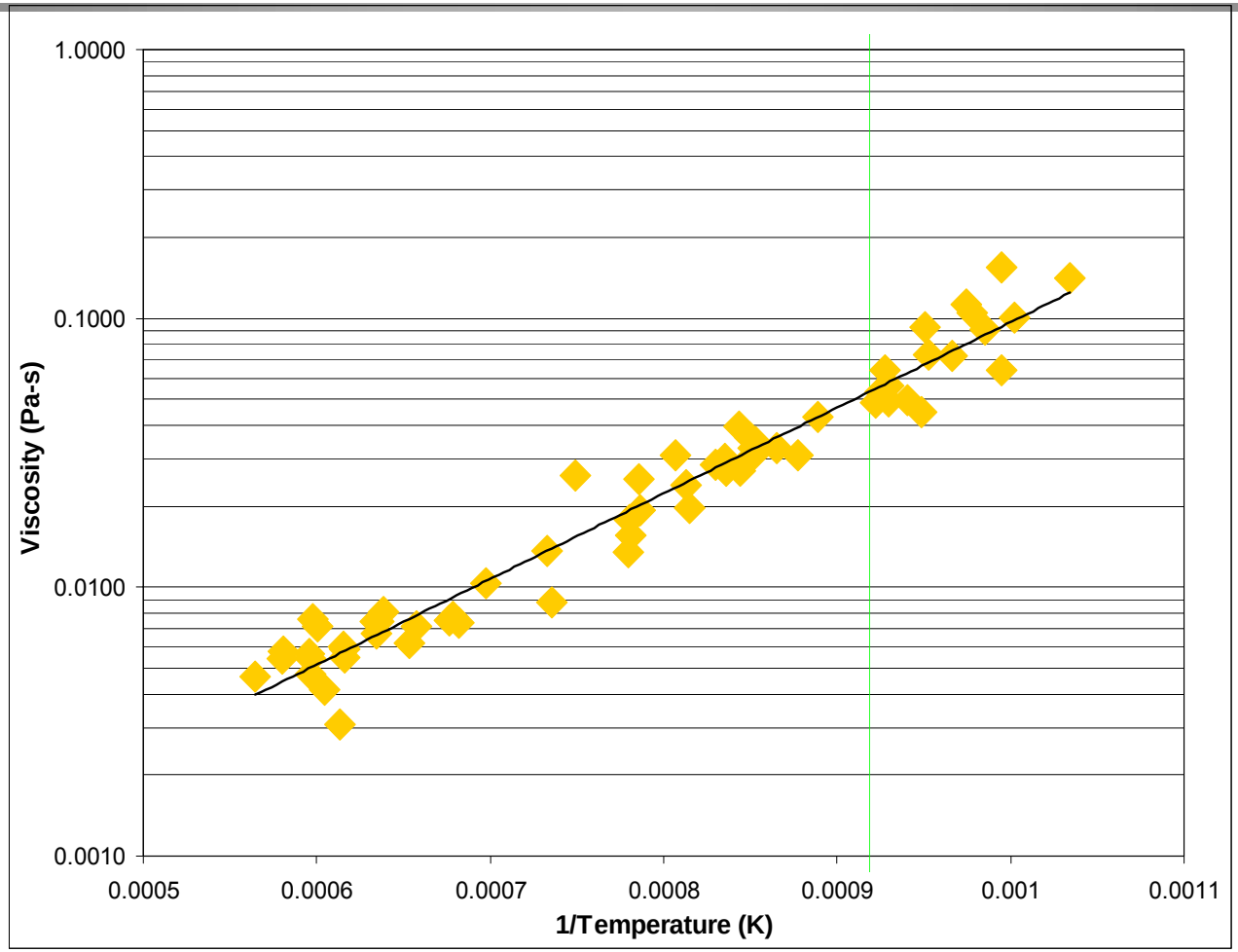


Filtered Oscillations

Nickel Sample, 46 mg, 5N pure, T=1290ºC (ΔT=165ºC)

K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

Viscosity of $Ti_{37}Zr_{42}Ni_{21}$



K.F. Kelton, A. Gangopadhyay (Wash. U. St. Louis), and R.W. Hyers (NASA MSFC)

Succinonitrile Purification Facility

Angela Shields and Louise Strutzenberg / SD46

The Succinonitrile (SCN) Purification Facility provides succinonitrile and succinonitrile alloys to several NRA selected investigations for flight and ground research at various levels of purity. The purification process employed includes both distillation and zone refining. Once the appropriate purification process is completed, samples are characterized to determine the liquidus and/or solidus temperature, which is then related to sample purity. The lab has various methods for measuring these temperatures with accuracies in the milliKelvin to tenths of milliKelvin range. The ultra-pure SCN produced in our facility is indistinguishable from the standard material provided by NIST to well within the stated +/- 1.5mK of the NIST triple point cells.

In addition to delivering material to various investigations, our current activities include process improvement, characterization of impurities and triple point cell design and development. The purification process is being evaluated for each of the four vendors to determine the efficacy of each purification step. We are also collecting samples of the remainder from distillation and zone refining for analysis of the constituent impurities. The large triple point cells developed will contain SCN with a melting point of 58.0642°C +/- 1.5mK for use as a calibration standard for Standard Platinum Resistance Thermometers (SPRTs).

Succinonitrile Processing

MSFC SCN Facility
SD46
4493/149
L. Strutzenberg
A. Shields

Investigations Supported to Date

- Equiaxed Dendritic Solidification Experiment (EDSE) – University of Iowa, C. Beckermann
- Dendritic Alloy Solidification Experiment (DASE) – University of Iowa, C. Beckermann
- Pore Formation and Mobility Investigation (PFMI) – MSFC, R. Grugel
- Evolution of Local Microstructures (ELMS) – Rensselaer Polytechnic Institute, M. Glicksman
- Interface Pattern Formation (IPF) – Iowa State University, R. Trivedi
- Stereo Imaging Velocimetry for Materials Science Experiments (SIV) – MSFC, N. Ramachandran

Additional Ongoing Activities

- Process Refinement
- Development of Triple Point Cells (TPC) for Standard Platinum Thermometer (SPRT) Calibration
- Characterization of Impurities by Vendor
- Materials Compatibility Assessments

Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

Flight experiment awarded by 94NRA

Principal Investigator: Dr. Ching-Hua Su, NASA/MSFC

Co-Investigators:

Prof. R. F. Brebrick, Marquette University
Dr. Burger, Fisk, University
Prof. M. Dudley, State University of New York
Prof. R. Matyi, University of Wisconsin (now at NIST)
Dr. N. Ramachandran, USRA/MSFC
Dr. M. Volz, NASA/MSFC

Industrial Guest Investigator:

Dr. Hung-Dah Shih, Texas Instruments

The objective of the project is to determine the relative contributions of gravity-driven fluid flows to the compositional distribution, incorporation of impurities and defects, and deviation from stoichiometry observed in the crystals grown by vapor transport as results of buoyancy-driven convection and growth interface fluctuations caused by irregular fluid-flows. ZnSe and related ternary compounds, such as ZnSeS and ZnSeTe, were grown by vapor transport technique with real time in-situ non-invasive monitoring techniques. The grown crystals were characterized extensively to correlate the grown crystal properties with the growth conditions. Significant effects of gravity vector orientation on the growth crystal morphology and point defect distribution were observed.

Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

Flight experiment awarded by 94NRA March 1996
Completed Science Concept Review (SCR) October 1998
Authorized to proceed toward Requirements Definition Review (RDR) October 1999

Principal Investigator: Dr. Ching-Hua Su, NASA/MSFC

Co-Investigators:

Prof. R. F. Brebrick, Marquette University

Dr. A. Burger, Fisk University

Prof. M. Dudley, State University of New York

Prof. R. Matyi, University of Wisconsin

Dr. N. Ramachandran, USRA/MSFC

Dr. M. Volz, NASA/MSFC

Industrial Guest Investigator:

Dr. Hung-Dah Shih, Texas Instruments

Other contributors:

Dr. S. Cha, University of Illinois at Chicago
Dr. S. Feth, University of Alabama at Huntsville/MSFC
Dr. M. George, University of Alabama at Huntsville
Dr. S. Lehoczky, NASA/MSFC
Dr. S. Motakef, Cape Simulations, Inc.
Dr. W. Palosz, USRA/MSFC
Dr. S. Sen, Santa Barbara Research Center
M. Smith/Dr. D. Hirshfeld/M. Weidenbeck,
New Mexico Tech/Sandia National Laboratories
Prof. L. Wang, University of Tennessee at Chattanooga

Technical support:

C. Bahr/D. Lovell/J. Quick, Sverdrup/Mevatec/MSFC

Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

1. Introduction and objectives
2. Thermodynamics of binary and ternary systems
3. Mass flux and heat treatments of starting materials
4. Crystal growth
5. Sample characterization
6. *In-situ* optical monitoring during growth
7. Theoretical calculations (Ramachandran et al. J. Crystal Growth 208 269 2000)

The problem:

To understand the relation between fluid phase processes (growth parameters) and defect and impurity incorporation in grown crystal

- **Experiments in low-gravity simplifies fluid process**
- **To study the incorporation and distribution of a point defect, an intentional dopant such as Cr, In or Al**
- **To study the generation of structural defect, such as a twin**

A list of II-VI semiconducting compounds grown by physical vapor transport (PVT) at MSFC

compounds	CdTe	ZnTe	CdS	ZnSe	ZnS
melting points (^oC)	1092	1292	1397	1526	1718
PVT growth temperature (^oC)	850	970	985	1100	1150

Scientific objectives:

1. To establish the relative contributions of gravity-driven fluid flows to (1) the non-uniform incorporation of impurities and defects and (2) the deviation from stoichiometry observed in the grown crystals as the results of buoyancy-driven convection and irregular fluid-flows caused by growth interface fluctuations (step bunching) and interface evolution.

2. To assess self-induced strain effects developed during processing at elevated temperatures and retained on cooling caused by the weight of the crystals from X-ray topography and by measuring the density and distribution of various crystalline defects.

By conducting numerical simulation of heat transfer, mass transport and growth kinetics using the evolutionary data (dimensions, interface shape, thermal field, physical properties, etc..) as inputs to obtain quantitative comparisons between the measured and calculated results of the vapor concentration distribution as well as the axial and radial segregation of impurities and native point defects in the grown crystals and thus help to simplify the complexity of the coupled mass transport and growth kinetics problem.

Determination of pertinent thermodynamic properties

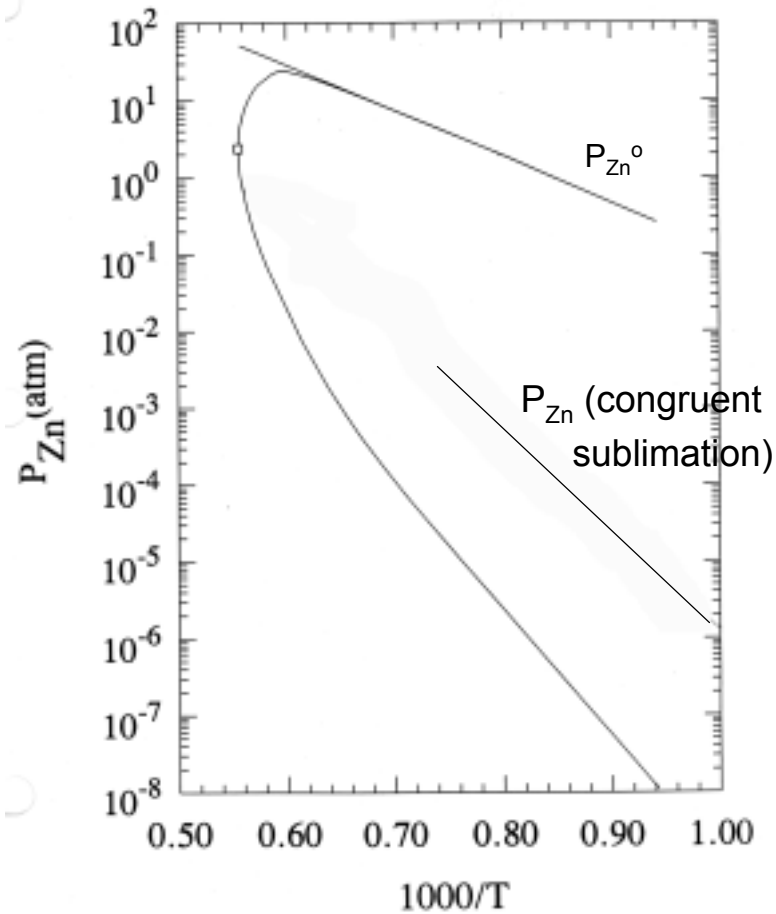
- **"Partial pressures of Zn and Se_2 over ZnSe(c) from optical density measurements".** **(Ph.D. Dissertation, H. Liu, Marquette University, 1995; Brebrick et al., High Temp. and Mater. Sci. 35 215,1996)**

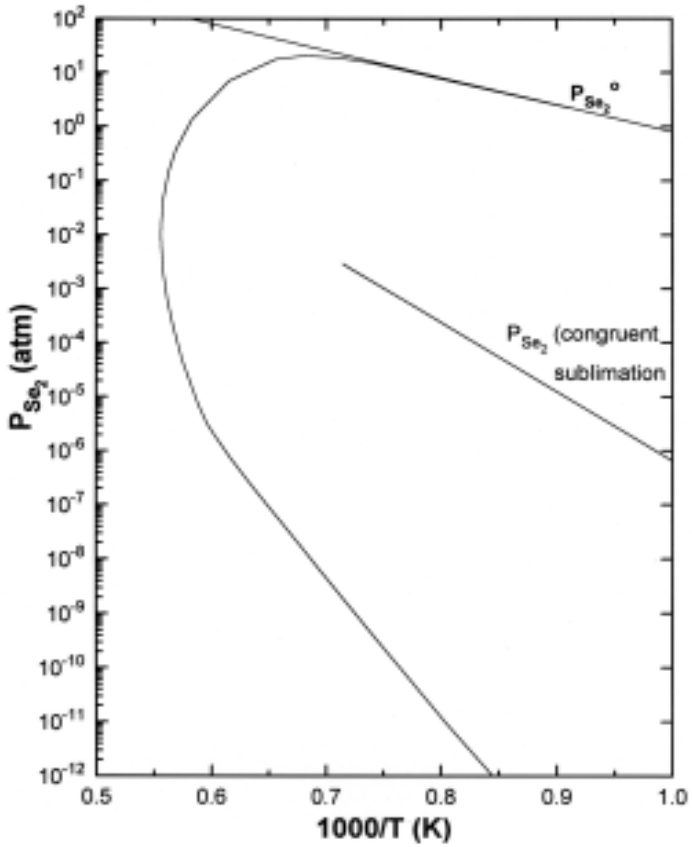
- **"Analysis of Zn-Se phase diagram and thermodynamic properties by an associated solution model for the liquid".** **(Brebrick et al., J. Phase Equilibria 17 495,1996)**

- **Ternary Zn-Se-Te phase diagram and thermodynamic property calculations.**

Calculated partial pressures along the three-phase curve for ZnSe(s)

At 1156 ^{o}C, P_{Zn} varies from 8.4 to 1.3×10^{-4} atm, P_{Se_2} varies from 20 to 5×10^{-9} atm and $\alpha = P_{Zn} / P_{Se_2}$ varies from 1.7×10^{9} to 6.5×10^{-6}





Optimization of mass flux by heat treatments of starting material

- **One dimensional diffusion model to identify the critical parameters in determining mass flux**
- **Heat treatments to control stoichiometry of source material**
- ***In-situ* dynamic measurements of mass flux (Y.-G. Sha et al., J. Crystal growth 146 42, 1995, C.-H. Su et al. J. Crystal Growth 183 519 1998)**
- **Measurements of residual gas pressure and composition**
- **Simultaneous measurements of partial pressure and mass flux in PVT of ZnSe (C.-H. Su et al., J. Crystal growth 166 736, 1996)**
- **Optimum heat treatment procedures for ZnSe starting material (C.-H. Su et al., J. Crystal growth 192 386, 1998)**
- **Mass flux in ZnSe-based ternary systems (Y.-G. Sha et al., J. Crystal growth 171 516, 1997)**

Summary of the mass flux optimization and heat treatments of ZnSe starting materials

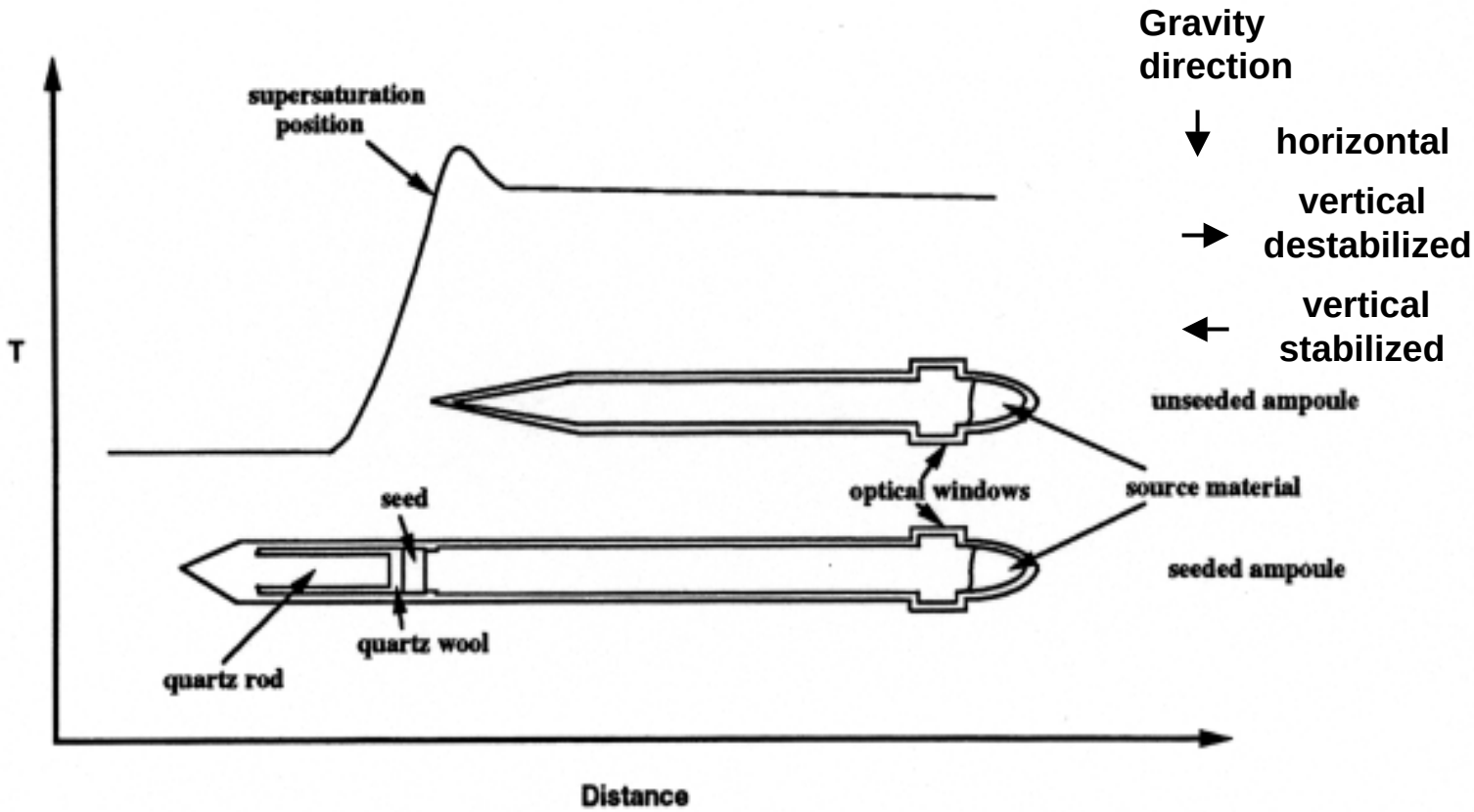
- **Mass flux measurements confirmed that the two parameters, the partial pressure ratio over source and the residual gas pressure, are critical in determining the mass flux.**
- **Various heat treatments were conducted to control the partial pressure ratio (vapor phase stoichiometry) over the source and the effectiveness of the treatments was evaluated by partial pressure measurements.**
- **Hydrogen reduction treatment was established to be effective in reducing the oxygen-related residual gas species.**
- **The optimum hydrogen reduction and vacuum treatment procedures were established for the source to maximize the mass flux in the ZnSe PVT process.**

Crystal growth by physical vapor transport

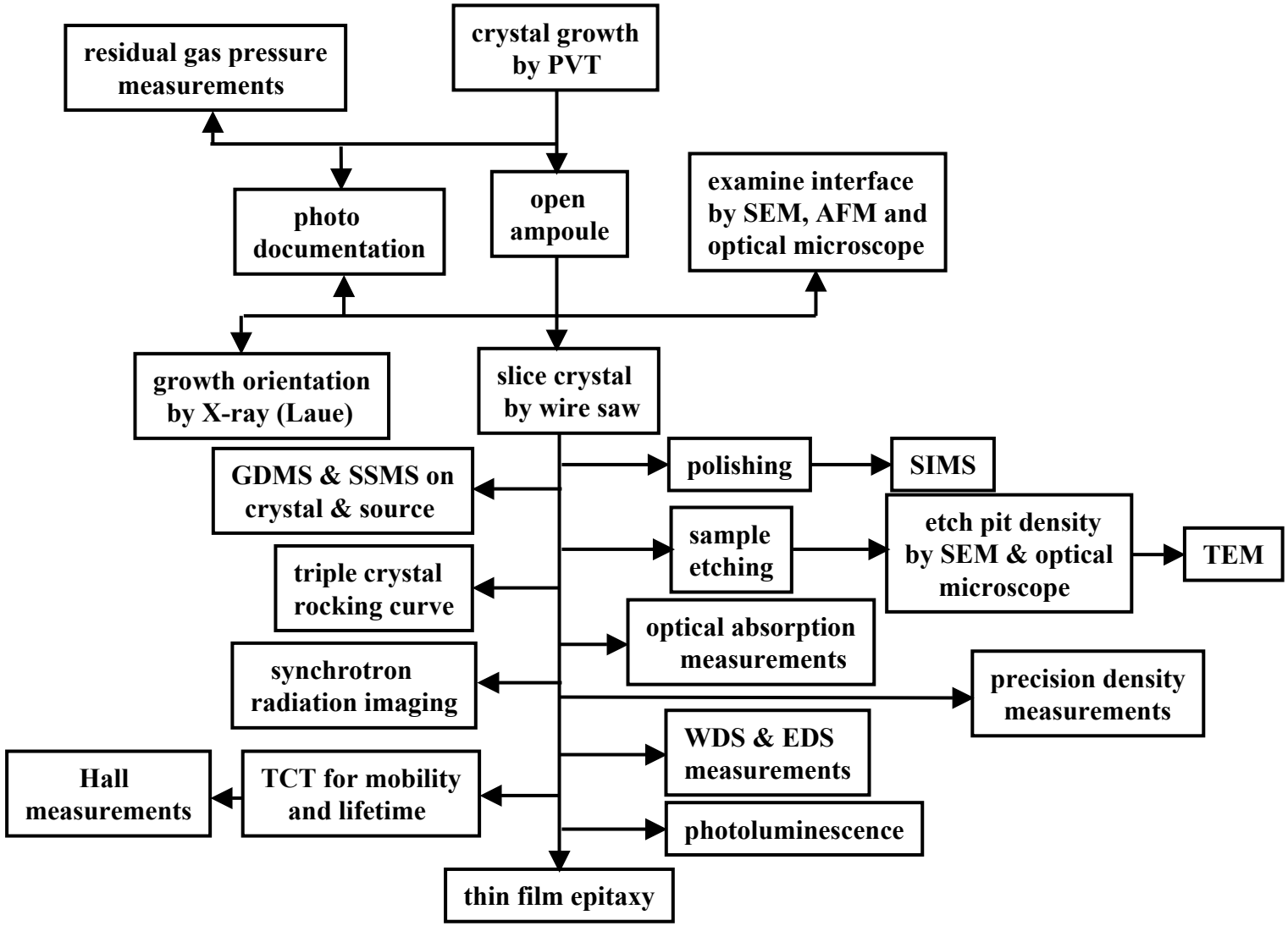
- **Self-seeded growth of ZnSe in vertical (stabilized and destabilized) and horizontal configurations. (C.-H. Su et al. J. Crystal growth 213 267 2000)**
- **Seeded growth of ZnSe in vertical and horizontal configurations**
- **Self-seeded growth of Cr-doped ZnSe in vertical and horizontal configurations. (C.-H. Su et al. J. Crystal growth 207 35 1999)**
- **Self-seeded growth of ZnSeTe in vertical and horizontal configurations. (C.-H. Su et al. J. Crystal Growth 216 104 2000)**
- ***In-situ* and real-time optical monitoring of seeded growth in a horizontal configuration. (C.-H. Su et al. J. Crystal Growth 209 687 2000)**

Schematics of temperature profile and initial ampoule positions

- The growth ampoules can be equipped with optical windows to confirm the stoichiometry of the starting material before growth.
- The thermal profile, with a maximum in the middle, was provided by a three-zone furnace with an adiabatic zone between central and cold zones.
- Growth was initiated by translating furnace to the right.



Flow chart of sample characterization plan



(C.-H. Su, J. Appl. Phys. 88 5148 2000)

Effects of gravity vector direction on self-seeded grown crystal morphology

- **Crystals grown in the horizontal configuration grew away from the ampoule wall with large areas of (110) facets tend to align parallel to the gravitational direction**

- **Crystals grown in the vertical configuration grew in contact with the wall to the full diameter of the ampoule and are usually unfaceted**

(C.-H. Su et al. J. Crystal Growth 208 237 2000)

Gravity effects on the point defect distributions in ZnSe crystals grown by physical vapor transport

I. Results from Secondary Ion Mass Spectroscopy (SIMS) mappings :

- For the horizontally grown self-seeded ZnSe crystal [Si] and [Fe] showed clear segregation toward the bottom on the wafer cut axially along the growth axis.
- For the vertically grown seeded ZnSe crystal [Si] and [Cu] showed segregation toward the edge of the wafer cut perpendicular to the growth axis .

(C.-H. Su et al. J. Crystal Growth 204 41 1999)

Gravity effects on the point defect distributions in ZnSe crystals grown by physical vapor transport (continued)

II. Mappings of photoluminescence (PL) near band edge intensity ratios indicated:

(1) All the horizontally-grown crystals showed the following trends in the radial and axial segregation of [Al] and [V_{Zn}] (zinc vacancy)

[Al] segregates radially toward the top and axially toward the first grown region and [V_{Zn}] segregates radially toward the bottom and axially toward the last grown region.

(2) The as-grown surface of the seeded vertically stabilized grown crystal showed [Al], [Li or/and Na] and [V_{Zn}] segregate radially toward the center.

(3) The as-grown surface of the self-seeded vertically destabilized grown crystal showed [Al] and [V_{Zn}] segregate radially without an apparent pattern.

(C.-H. Su et al. J. Crystal Growth 224 32 2001)

Summary of *in-situ* optical monitoring results

- **Growth furnace, optical monitoring set-up and growth ampoule design for in-situ optical monitoring during the PVT growth of ZnSe were constructed and optimized.**

- **Results of the partial pressure measurements during growth of sample ZnSe(IS)-5:**

  P_{Se_2} measured along the ampoule length were inconsistent with one-dimensional diffusion model.

  The source composition shifted toward Se-rich during the run the grown crystal was more Zn-rich than the source.

Structural Fluctuation and Thermophysical Properties of Molten II-VI Compounds

A ground-based project awarded by 98NRA

Principal Investigator: Dr. Ching-Hua Su, SD46 NASA/MSFC

Co-Investigators:

Dr. Shari Feth, University of Alabama in Huntsville/MSFC
Dr. Sandor Lehoczky, SD40, NASA/MSFC
Dr. Herb Mook, Oak Ridge National Laboratory
Prof. Rose Scripa, University of Alabama at Birmingham
Dr. Shen Zhu, USRA/MSFC

The objectives of the project is to conduct ground-based experimental and theoretical research on the structural fluctuations and thermophysical properties of molten II-VI compounds to enhance the basic understanding of the existing flight experiments in microgravity materials science programs and to study the fundamental heterophase fluctuations phenomena in these melts by:

1) conducting neutron scattering analysis and measuring quantitatively the relevant thermophysical properties of the II-VI melts such as viscosity, electrical conductivity, thermal diffusivity and density as well as the relaxation characteristics of these properties to advance the understanding of the structural properties and the relaxation phenomena in these melts and

2) performing theoretical analyses on the melt systems to interpret the experimental results.

All the facilities required for the experimental measurements have been procured, installed and tested. A relaxation phenomenon, which shows a slow drift of the measured thermal conductivity toward the equilibrium value after cooling of the sample, was observed for the first time. An apparatus based on the transient torque induced by a rotating magnetic field has been developed to determine the viscosity and electrical conductivity of semiconducting liquids. Viscosity measurements on molten tellurium showed similar relaxation behavior as the measured diffusivity. Neutron scattering experiments were performed on the HgTe and HgZnTe melts and the results on pair distribution showed better resolution than previous reported.

Structural fluctuations and Thermophysical Properties of Molten II-VI Compounds

A ground-based project awarded by 98NRA on January 2000

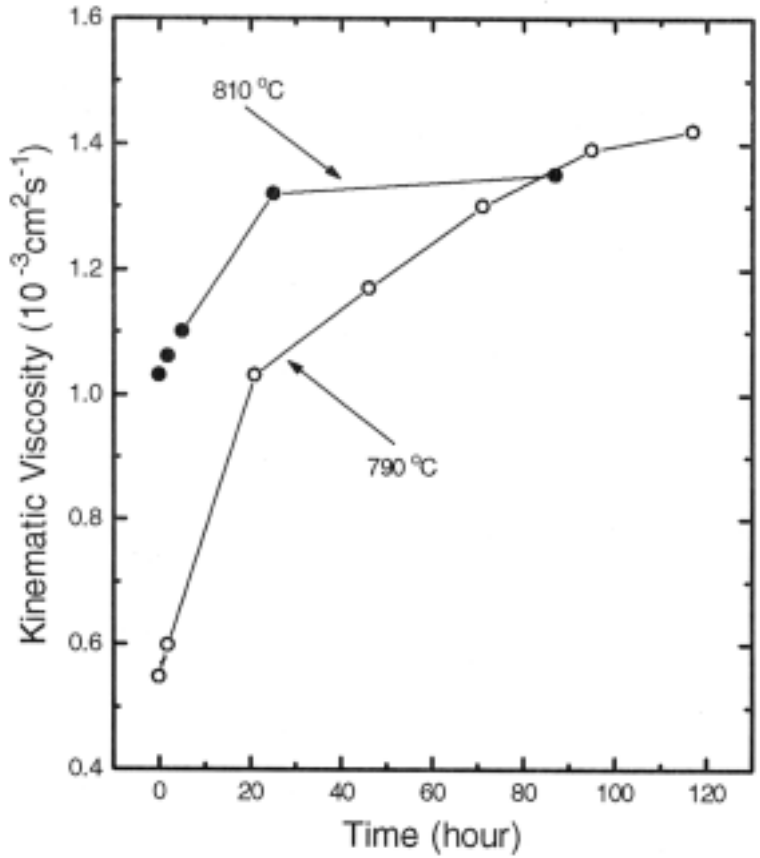
Principal Investigator:

- **Dr. Ching-Hua Su, SD46 NASA/MSFC**

Co-Investigators:

- **Dr. Shari Feth, University of Alabama in Huntsville/MSFC**
- **Dr. Sandor Lehoczky, SD40, NASA/MSFC**
- **Dr. Herb Mook, Oak Ridge National Laboratory**
- **Dr. Rose Scripa, University of Alabama at Birmingham**
- **Dr. Shen Zhu, USRA/MSFC**

An unexpected time drift of the measured viscosity, which shows a slow relaxation phenomena at temperatures near the liquidus point of $Hg_{0.84}Zn_{0.16}Te$ melt, was reproducibly observed.



Time variation of the measured viscosity after cooling from 850°C to the prescribed temperatures of 810°C and 790°C.

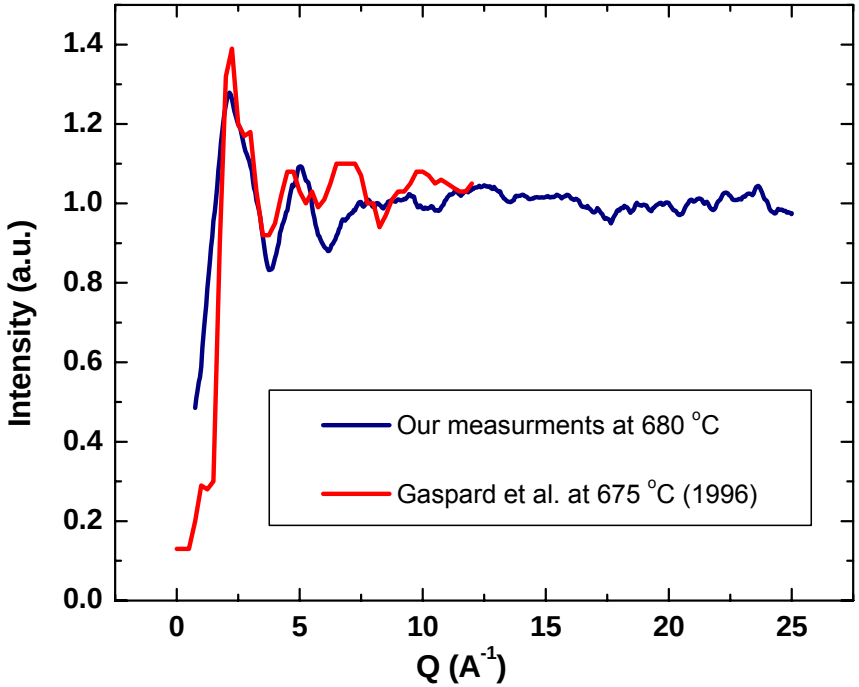
Scientific Objectives:

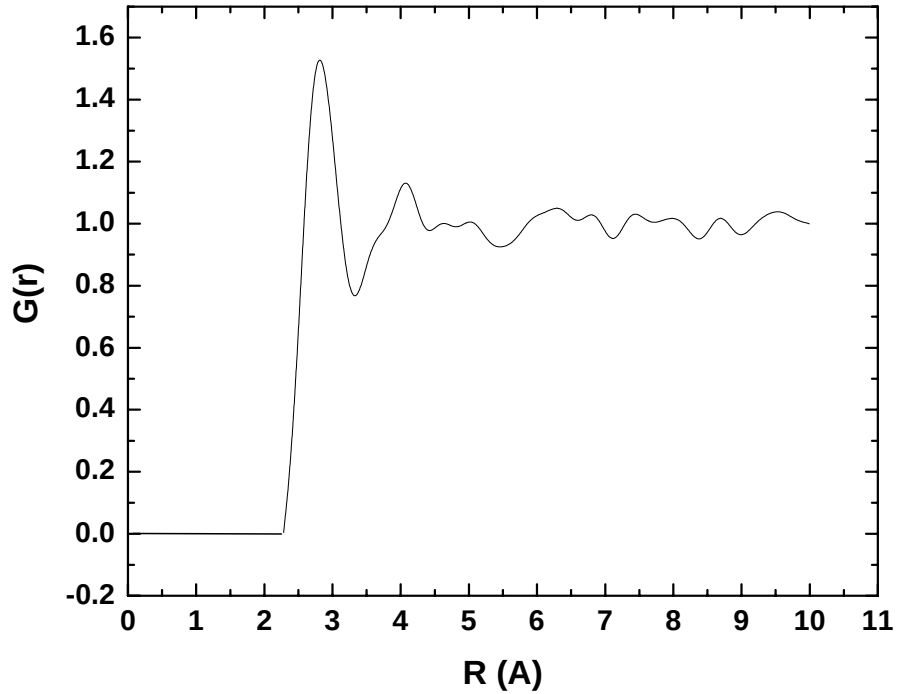
To conduct ground-based experimental and theoretical research on the structural fluctuations and thermophysical properties of molten II-VI compounds to enhance the basic understanding of the existing flight experiments in microgravity materials science programs ("Crystal Growth of Selected II-VI Semiconducting Alloys by Directional Solidification" and "Growth of Solid Solution Single Crystals") and to study the fundamental heterophase fluctuations phenomena in these melts by:

- **Conducting neutron scattering analysis and measuring quantitatively the relevant thermophysical properties of the melts such as viscosity, electrical conductivity, thermal diffusivity and density as well as the relaxation characteristics of these properties to advance an understanding of the structural properties and the relaxation phenomena in these melts and**
- **Performing thermodynamic analyses on the melts to interpret the experimental results.**

(a) Neutron scattering analysis:

Neutron scattering will be employed to study the heterophase fluctuations near the liquidus temperature as well as at higher temperatures in the HgTe binary as well as in the HgCdTe and HgZnTe pseudobinary melts of various compositions. The samples will be prepared inside a fused silica crucible. The initial experiments will involve the determination of the radial distribution function using a low wavelength or high momentum transfer setup. Two sets of experimental measurements will be performed: measurements as a function of time near the liquidus point and measurements as a function of temperature from the liquidus to higher temperatures. The results will provide basic information on the liquid structure and will dictate the selection of further experiments.





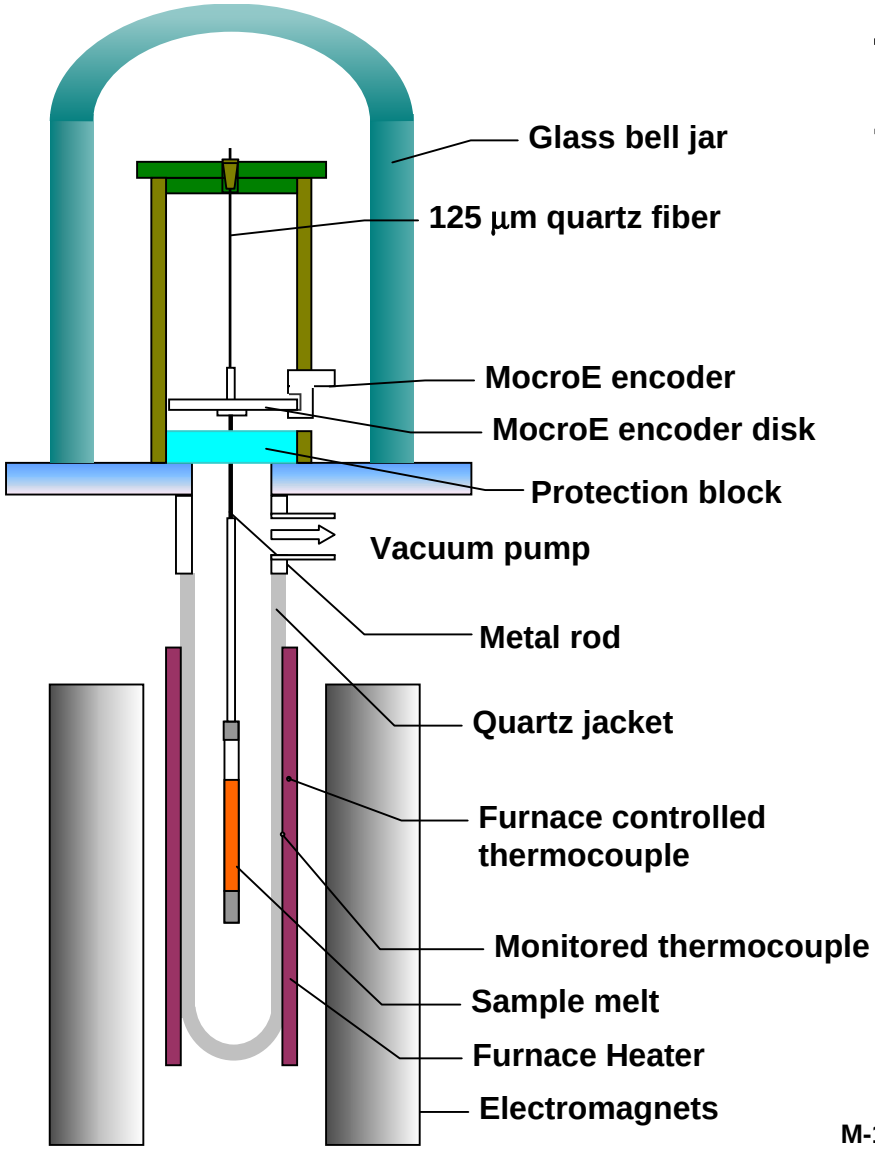
Neutron scattering experiments on the HgTe and $Hg_{0.84}Zn_{0.16}Te$ melts were performed at the Glass Liquid and Amorphous Materials Diffractometer (GLAD), Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory (ANL). Three neutron scattering spectra of the HgTe sample were taken, first at 680°C, 10°C above its melting point, then at 800°C before taken at 680°C again. No distinguishable difference was observed among these three spectra. Our results on the structure factor (left) shows agreements with Gaspard *et al* below 5A^{-1} and extends to higher wavenumber, which results in the pair distribution function (right) in general agreement with that of Gaspard *et al* except a better resolution at larger interatomic distance, indicating a higher degree in long-range order.

(b) Viscosity and electrical conductivity:

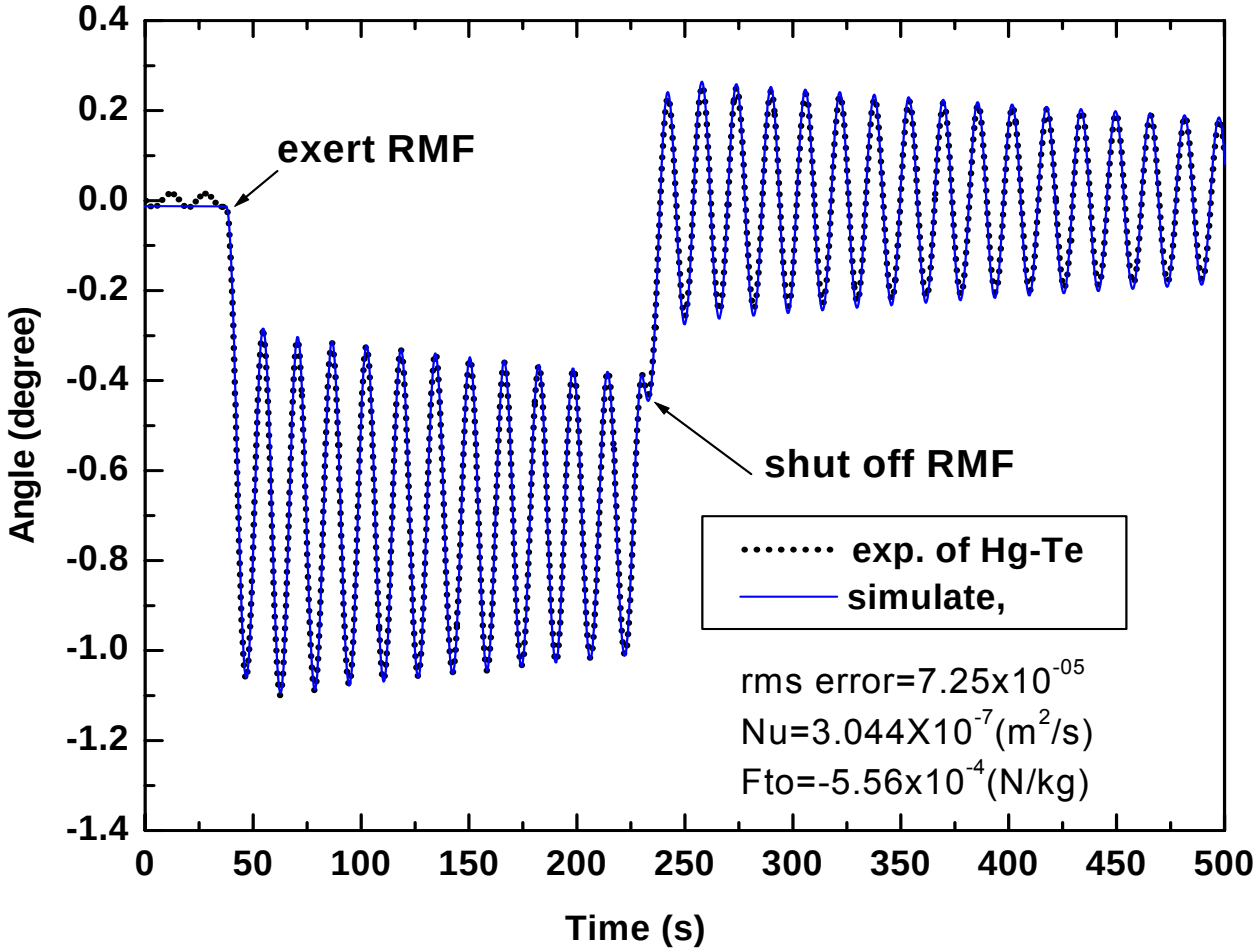
It is proposed to employ the Transient Torque technique generated by a rotating magnetic field technique to monitor the viscosity and electrical conductivity of Te, HgTe, HgCdTe and HgZnTe melts under two different experimental conditions: (1) the viscosity and electrical conductivity measurements as a function of time near the liquidus point; i.e. about 30°C below and above the liquidus temperature and (2) the measurements as a function of temperature from the liquidus to higher temperatures. The results will provide basic information on the heterophase fluctuations near the liquidus temperature as well as the semiconductor-metal transition in the melt over a wide temperature range.

- **C. Li, R. N. Scripa, H. Ban, B. Lin, Ching-Hua Su, S. L. Lehoczky, S. Feth and S. Zhu, "Technique for Determining the Viscosity and Electrical Conductivity of Semiconducting Liquids", to be presented at CIMTEC (International Conference on Modern Materials and Technologies), 2002, Florence, Italy, July 14-19, 2002.**
- **Bochuan Lin, Chao Li, Heng Ban, Rose Scripa, Shen Zhu, Ching-Hua Su, and S. L. Lehoczky, "Theory and Simulation of a Novel Viscosity Measurement Method for high Temperature Semiconductor:, to be presented at 2002 ASME (International Mechanical Engineering Congress and Exposition), New Orleans November 17-22, 2002.**

Transient Torque Viscometer

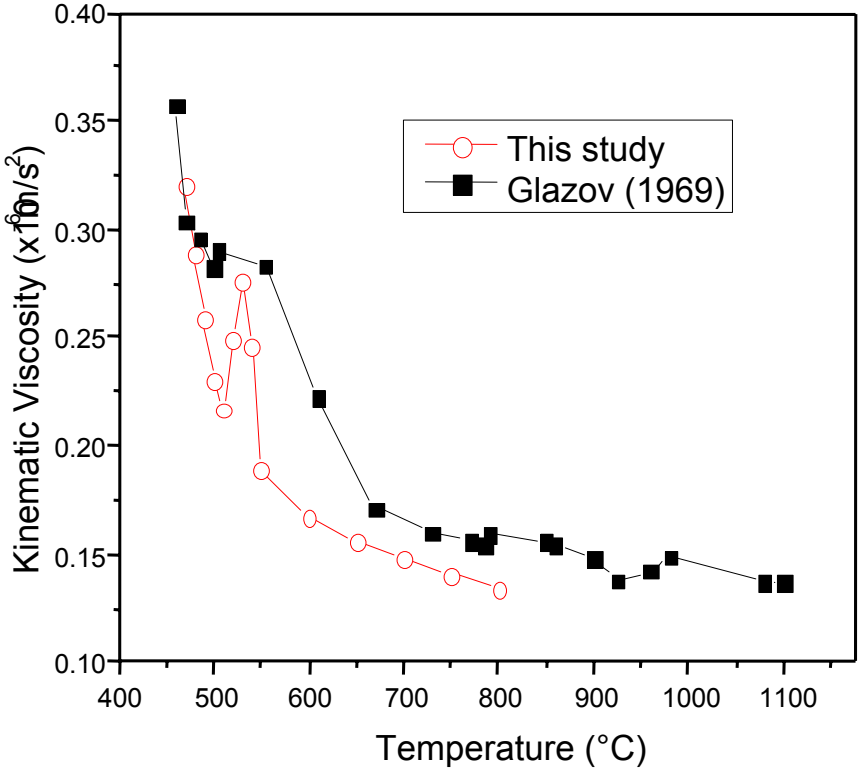


The TTV consists of an ampoule filled with the measured electrically conducting or semiconducting melt. The ampoule is suspended by a 125μm thin quartz fiber. The RMF induces small rotation behavior of ampoule. The magnitude of the angular deflection activities of the ampoule is conveniently measured by the Micro-E optical encoder disk.

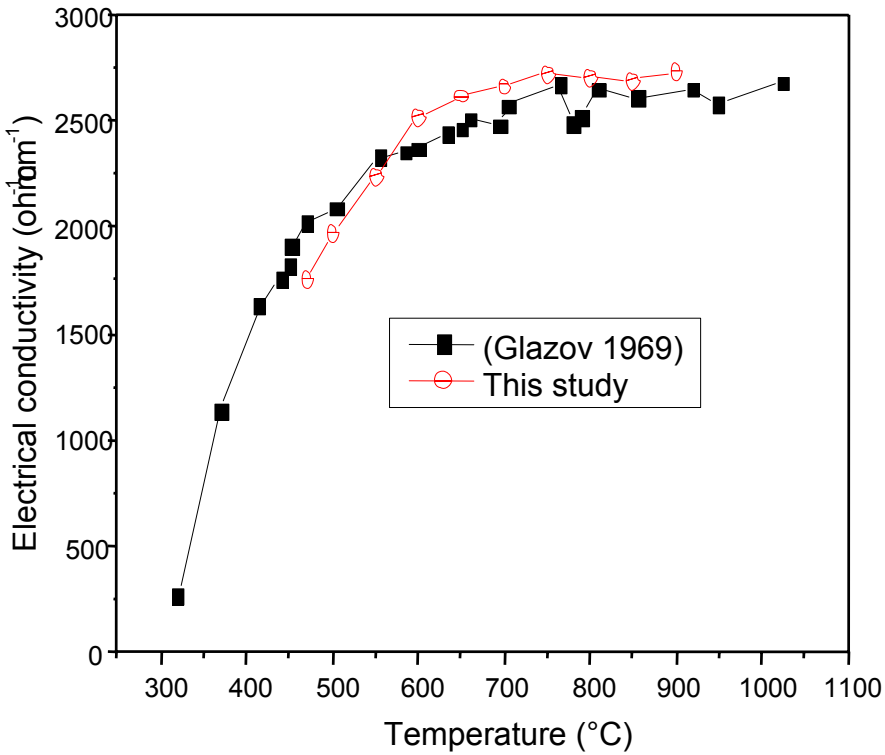


The angular deflection vs. time for HgTe melt. The dotted line is the experimental results and the blue solid line the calculated results.

Results



Viscosity of Te melt

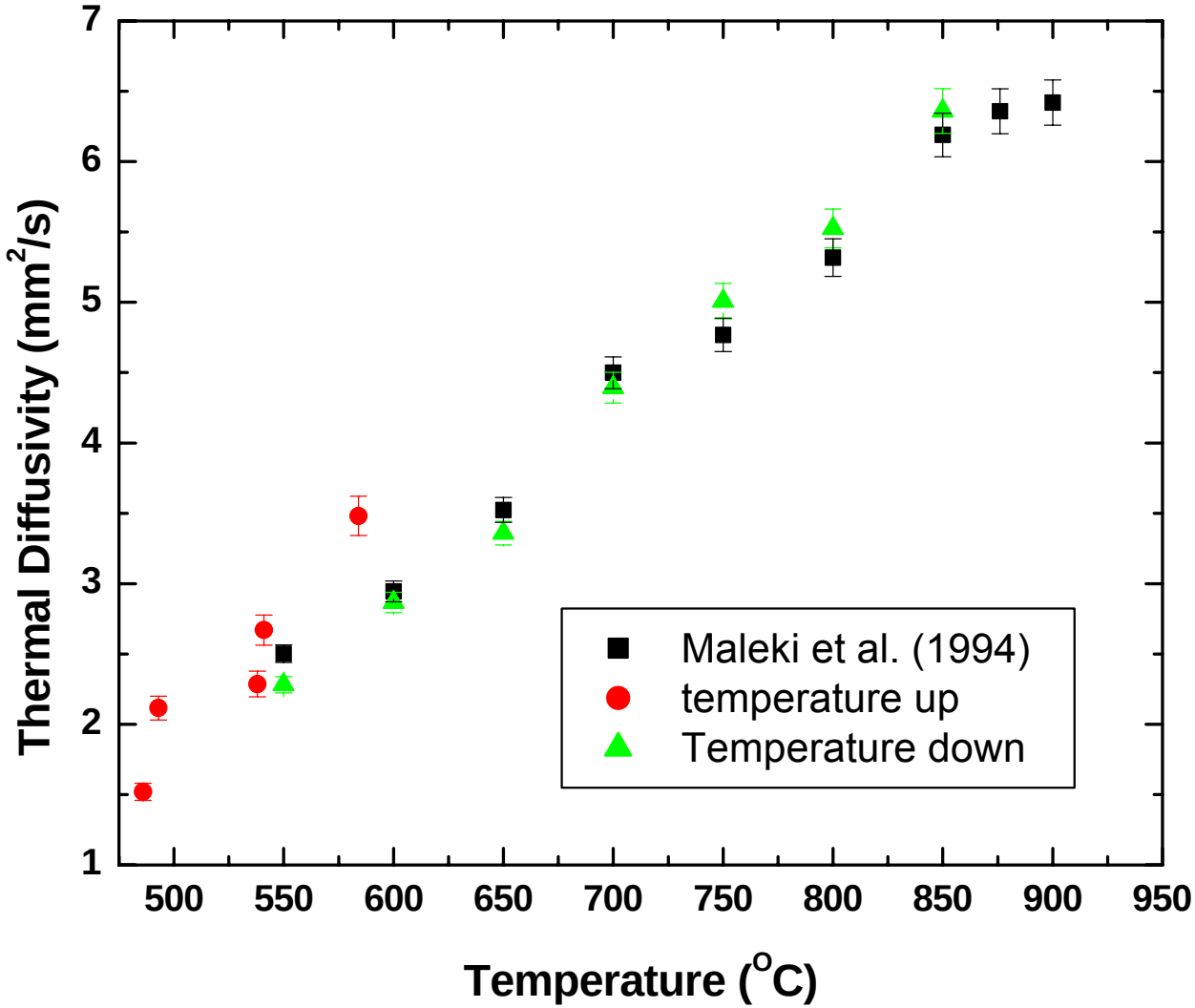


Electrical conductivity of Te melt

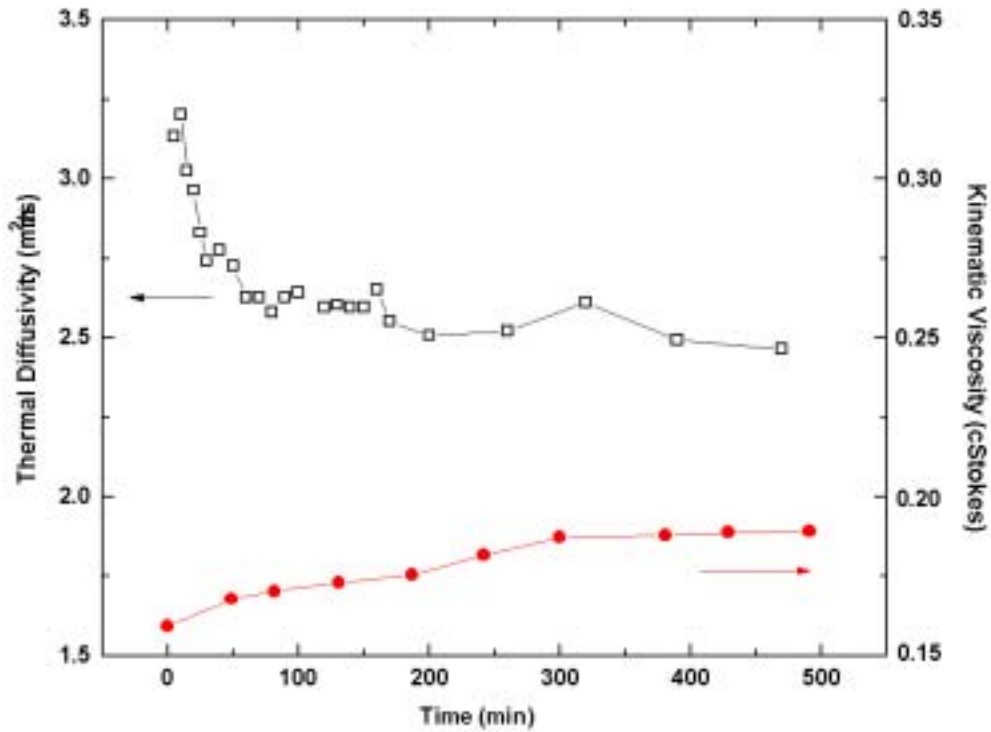
(c) Thermal diffusivity measurements:

A dynamic measurement of the thermal diffusivity using the laser flash method has been employed previously to determine the thermal conductivity of various composite materials as well as those systems that have to be enclosed in closed ampoules due to their high vapor pressures or toxic nature. In this method, the front surface of a small disk-shaped sample is subjected to a very short burst of radiant energy from a laser pulse with a radiation time of 1ms or less. The resulting temperature rise of the rear surface of the sample is measured and thermal diffusivity values calculated from the data of temperature rise versus time. Two sets of experimental conditions will be performed: the measurements as function of time near the liquidus point and measurements as function of temperature from the liquidus to higher temperatures. The results will provide basic information on the heterophase fluctuations near the liquidus temperature as well as on the semiconductor-metal transition over a wide temperature range.

Shen Zhu, C. Li, Ching-Hua Su, B. Lin, H. Ben, R. N. Scripa, and S. L. Lehoczky, "Characterizing Thermal Properties Of Melting Semiconductors: Thermal Diffusivity Measurements and Simulation", to be presented at the Fourteenth American Conference on Crystal Growth and Epitaxy (ACCGE-14), Seattle, Washington August 5-9, 2002.



Measured thermal diffusivity of Te melt

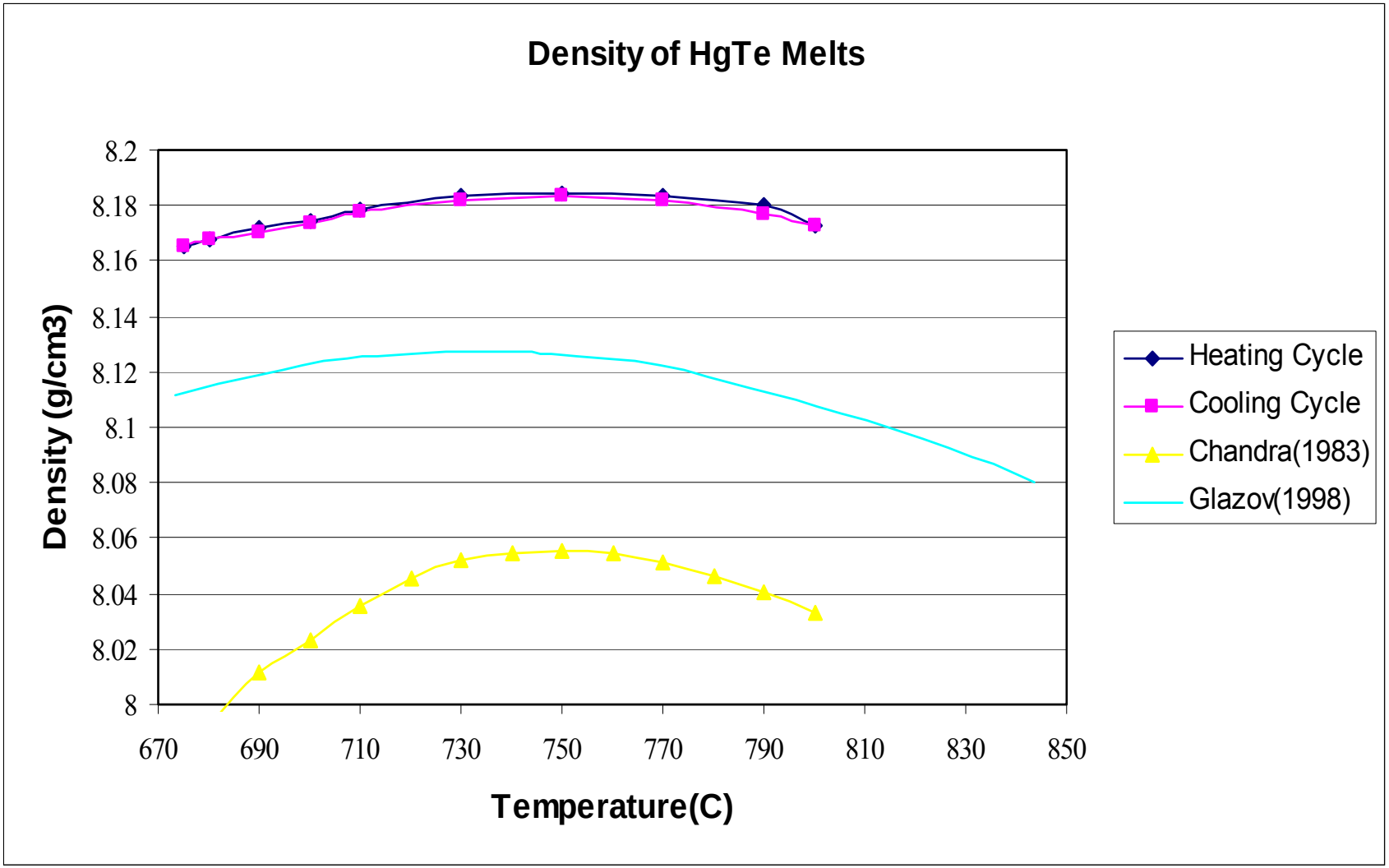


Measured thermal diffusivity and viscosity of Te melt as a function of time after the melt was quenched from 900°C to 560°C. It is the first time that the relaxation phenomenon was observed on an element of II-VI compounds.

C.Li, C-H Su, R.N. Scripa, B. Lin, H. Ban, and S.L. Lehoczky, "Observed Relaxation Phenomena in the Viscosity of Liquid Tellurium", to be presented at the Fourteenth American Conference on Crystal Growth and Epitaxy (ACCGE-14), Seattle, Washington August 5-9, 2002

(d) Density and volume expansion coefficient:

The measurements will be carried out in thermometer-shaped fused silica ampoules, which were placed vertically inside a transparent furnace and the meniscus heights measured using a cathetometer. It is proposed to measure the density of these pseudobinary melts with specific improvements in the ampoule design, the isothermality and the stability of the furnace. Beside HgCdTe and HgZnTe melts, the two sets of measurements, as described in previous sections, will be performed on the HgTe binary system.



The measured density of HgTe melt confirmed the anomalous behavior of a maximum in density vs. temperature and is about 0.6% higher than the results of Glazov et al. by γ-rayattenuation. (The usual error caused by trapped bubbles result in lower density.) No relaxation behavior was found.

Theoretical

A theory was proposed to explain the relaxation behavior of the HgZnTe melt. It assumes that the polymerization reaction of Te chains with second order kinetics that increase the molecular weight, and decomposition reaction with first order kinetics that inactivate the chains. Using the standard semi-empirical relation between polymer average molecular weight and viscosity, the viscosity relaxation curve can be fitted to get the reaction constants.

(Y. W. Kim, J. K. Baird, Ching-Hua Su, and S. L. Lehoczky, to be published in Phys. Chem. Of Liquids)

Laboratory and In-Flight, *In-Situ* X-ray Imaging and Scattering Facility for Materials, Biotechnology and Life Sciences

Instrument Technology Development (ITD) project

Co Principal Investigators:

Dr. Ching-Hua Su, MSFC **Prof. A. A. Chernov, USRA/MSFC**

Co-Investigators:
Dr. Zhengwei Hu, USRA/MSFC
Dr. Martin Volz, NASA/MSFC
Dr. Bill R. Thomas, USRA/MSFC

We propose a multifunctional x-ray facility for the Materials, Biotechnology and Life Sciences Programs to visualize formation and behavior dynamics of materials, biomaterials, and living organisms, tissues and cells. The facility will combine X-ray topography, phase micro-imaging and scattering capabilities with sample units installed on the goniometer. This should allow, for the first time, to monitor under well defined conditions, *in situ*, in real time: creation of imperfections during growth of semiconductors, metal, dielectric and biomacromolecular crystals and films, high-precision diffraction from crystals within a wide range of temperatures and vapor, melt, solution conditions, internal morphology and changes in living organisms, tissues and cells, diffraction on biominerals, nanotubes and particles, radiation damage, also under controlled formation/life conditions.

The system will include an ultrabright X-ray source, X-ray mirror, monochromator, image-recording unit, detectors, and multipurpose diffractometer that fully accommodate and integrate furnaces and samples with other experimental environments. The easily adjustable Laboratory and In-flight versions will allow monitoring processes under terrestrial and microgravity conditions. The in-flight version can be made available using a microsource combined with multilayer or capillary optics.

Laboratory and In-flight *In Situ* X-ray Imaging and Scattering Facility for Materials, Biotechnology and Life Sciences

Instrument Technology Development (ITD) project awarded on February 2001

Co Principal Investigators:

Dr. Ching-Hua Su
NASA/Marshall Space Flight Center

Prof. A. A. Chernov
Universities Space Research Association

Co-Investigators:

Dr. Zhengwei Hu
Universities Space Research Association

Dr. Martin Volz
NASA/Marshall Space Flight Center

Dr. Bill R. Thomas
Universities Space Research Association

PROPOSED INSTRUMENT:

A multi-functional X-ray facility to visualize formation and behavior dynamics of imperfections in materials, biomaterials, and living organisms, tissues and cells.

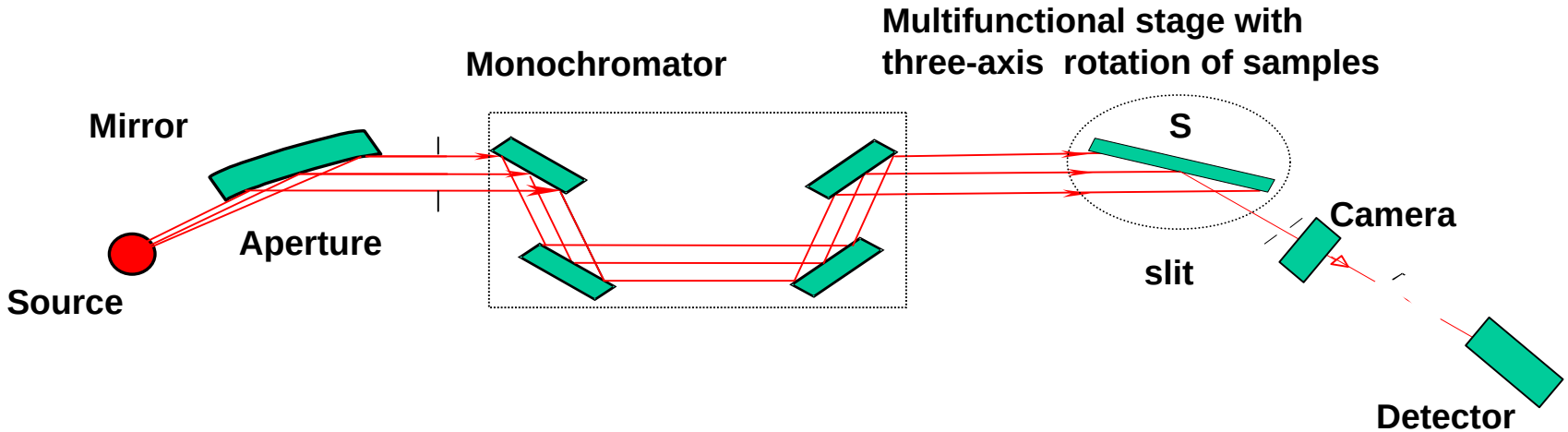
SIGNIFICANCES:

1. **The first *in situ* and real time X-ray imaging facility.**

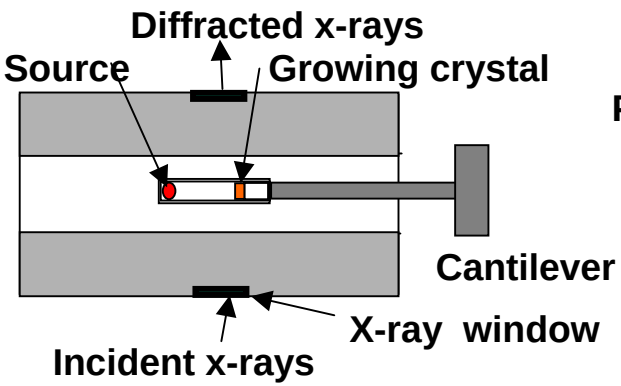
2. **The proposed instrument combines X-ray topography, phase micro-imaging and scattering capabilities and is capable of performing:**

- **Reflection X-ray topography for analyses of strain, twins, stacking faults, dislocations, point defects and grains in semiconductors, metals and oxide crystals, crystalline or polymer films, especially at elevated temperatures;**
- **Transmission X-ray topography for analogous studies of biomacromolecular crystals, bulk polymers and films;**
- **Diffraction and high precision rocking curve measurements on crystals, diffraction assessment of polycrystalline biomineralization and nanoparticles;**
- **Phase imaging to observe subtle density variations in living organisms, tissues, cells during processes such as bone formation/loss, radiation damage, morphological changes and processes in optical opaque biological objects.**

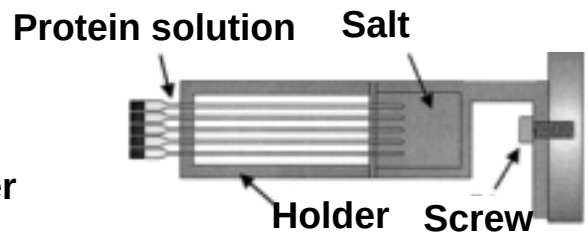
Laboratory and In Flight In-Situ X-ray Imaging and Scattering Facility



Schematic and deliverables of the proposed x-ray imaging and scattering Facility



(a)



(b)

(c)

Versatile sample stage and goniometer can accommodate (a) high temperature crystal growth furnace (b) growth attachments for proteins and (c) living cells

EVOLUTION OF LOCAL MICROSTRUCTURES: SPATIAL INSTABILITIES IN COARSENING CLUSTERS

Martin E. Glicksman[1], Donald O. Frazier[2], Jan R. Rogers[2], and William K. Witherow[2]

Rensselaer Polytechnic Institute[1], NASA, Marshall Space Flight Center[2]

Diffusion-limited capillarity-driven coarsening of precipitates is an important and intensively studied phenomenon. The classic coarsening theory developed by Lifshitz and Syozov and Wagner (LSW theory) is limited to infinitesimally small volume fractions, V_v, therefore neglects all direct inter-particle interactions. This work uses modeling and holographic imaging to compare coarsening rates in "high" volume fraction versus low volume fraction microstructures by observing mixed-dimensional droplets (spherical caps on a surface coarsening by two-dimensional diffusion) during ground-based investigations. The method involves filling a cell with selected homogeneous parent phase, and cooling below the consolute temperature to the isopycnic temperature in the two-phase region of a monotectic system. A microgravity holographic experiment is required for three-dimensional observations to minimize sedimentation during long-term coarsening.

Determination of sizes and positions of the many droplets in the holographic images requires automation. We have developed software for automated data analysis, and demonstrated good agreement between regenerated maps and scaled photographs of the original holograms for mixed-dimensional coarsening.

The results of these experiments were presented in a formal microgravity Science Concept Review (SCR) on December 18, 2000.

ELMS SCIENCE TEAM

RPI (Theory and modeling):

- Martin E. Glicksman (Lead)
- K-G Wang (Computational Methods)

MSFC(Experimental Development):

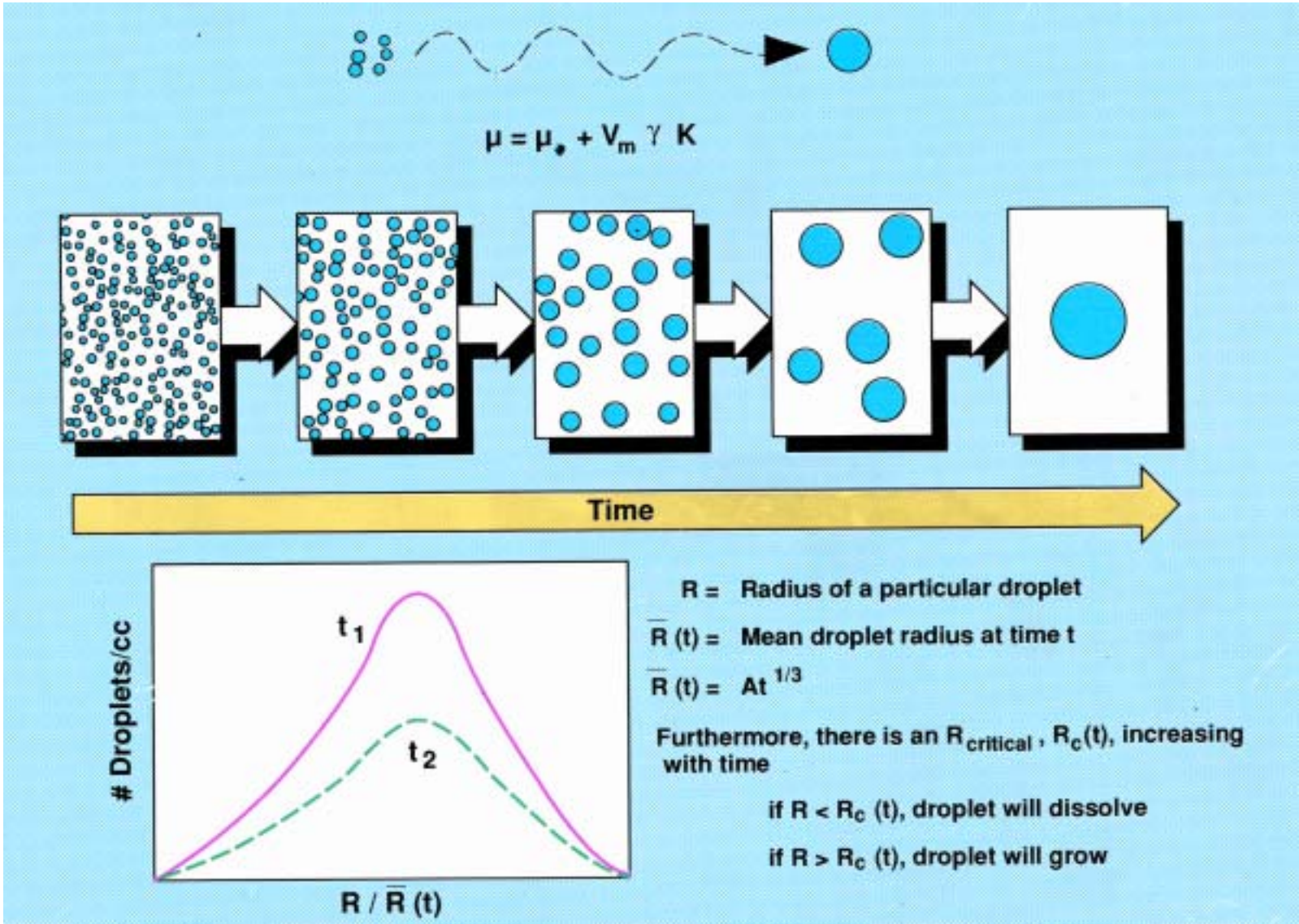
- Donald O. Frazier (Lead)
- Patton Downey (Modeling)
- Jan R. Rogers (Experimental Methods)
- William K. Witherow (Optics)

East West Enterprises:

- Ramarao Inguva (Image Processing/Data Extraction Methods)

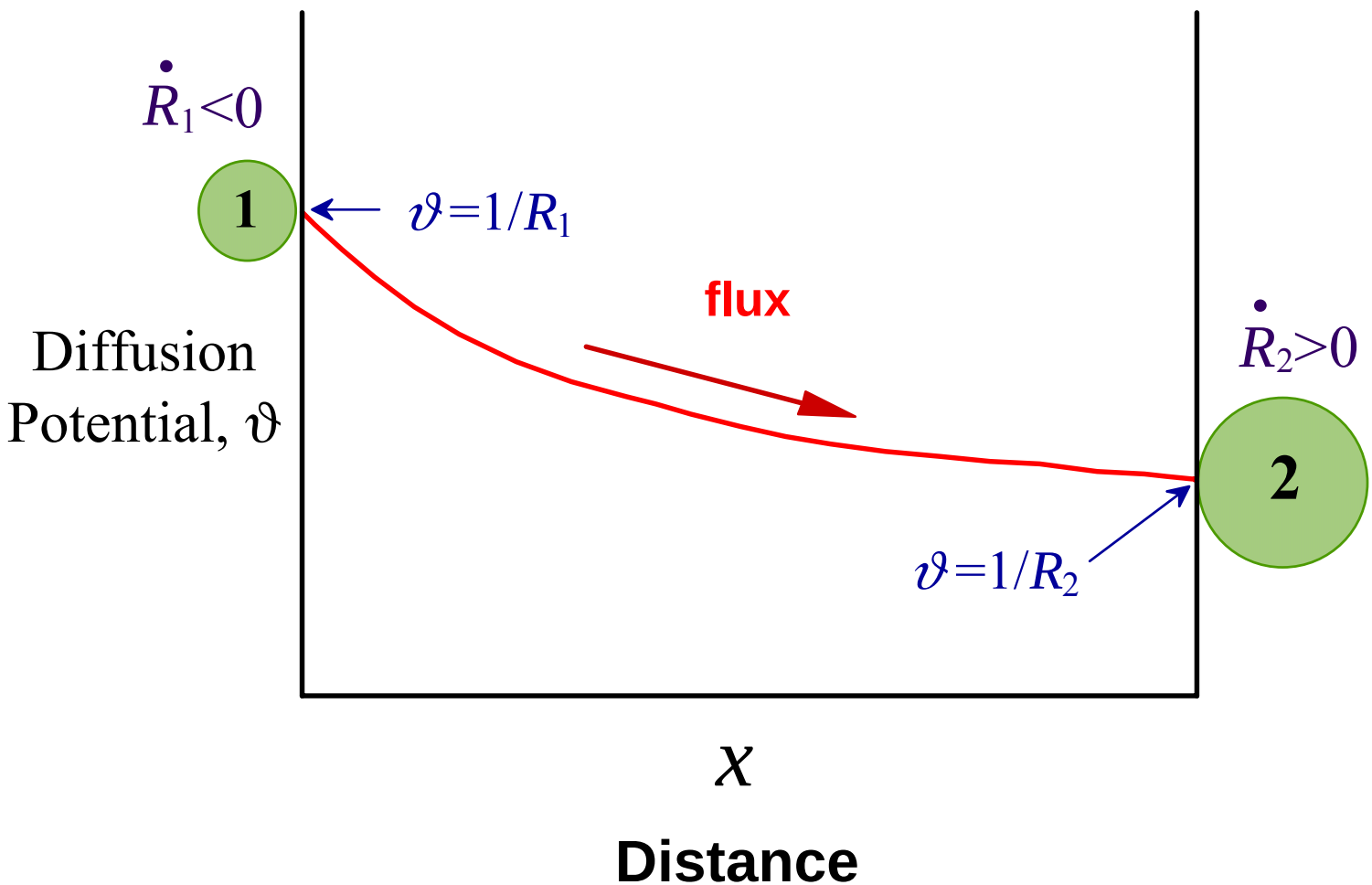
Ostwald Ripening

- **Ripening, or phase coarsening, is a *diffusional process* arising in a heterogeneous material in which the phase components are polydisperse.**
- **Growth occurs because the *flux of solute*, driven by chemical potential gradients at the interface, is *a function of particle size*.**
- **The *competitive kinetics* of the process dictate that larger particles grow at the expense of smaller ones.**



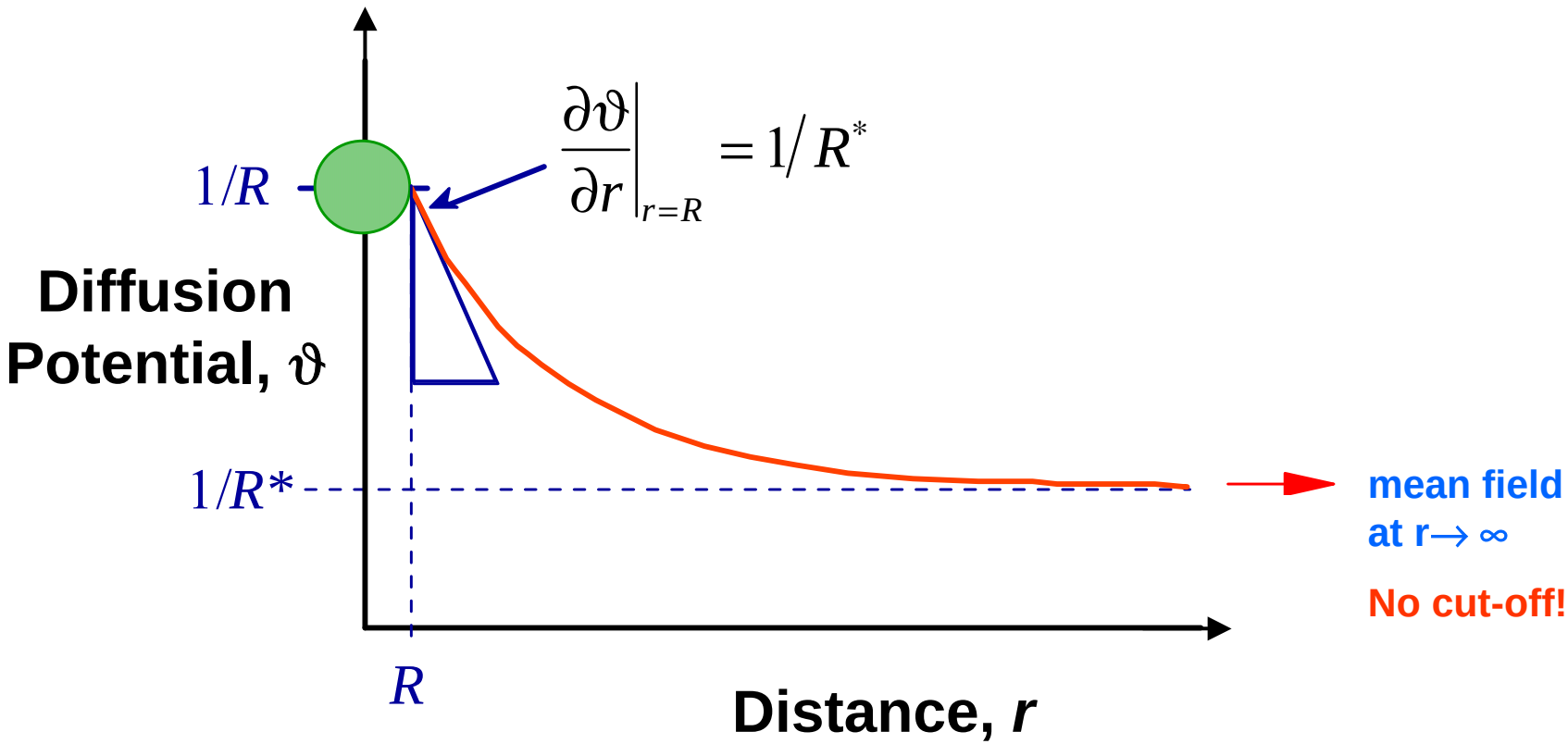
Where μ is the chemical potential of droplet of radius R, μ. is chemical potential of very large droplet having zero curvature (planar surface), V_m is the molar volume of the droplet phase, γ is the interfacial energy of phases, and **K** is the curvature of droplet of radius R (1/R).

Capillary-Driven Diffusion



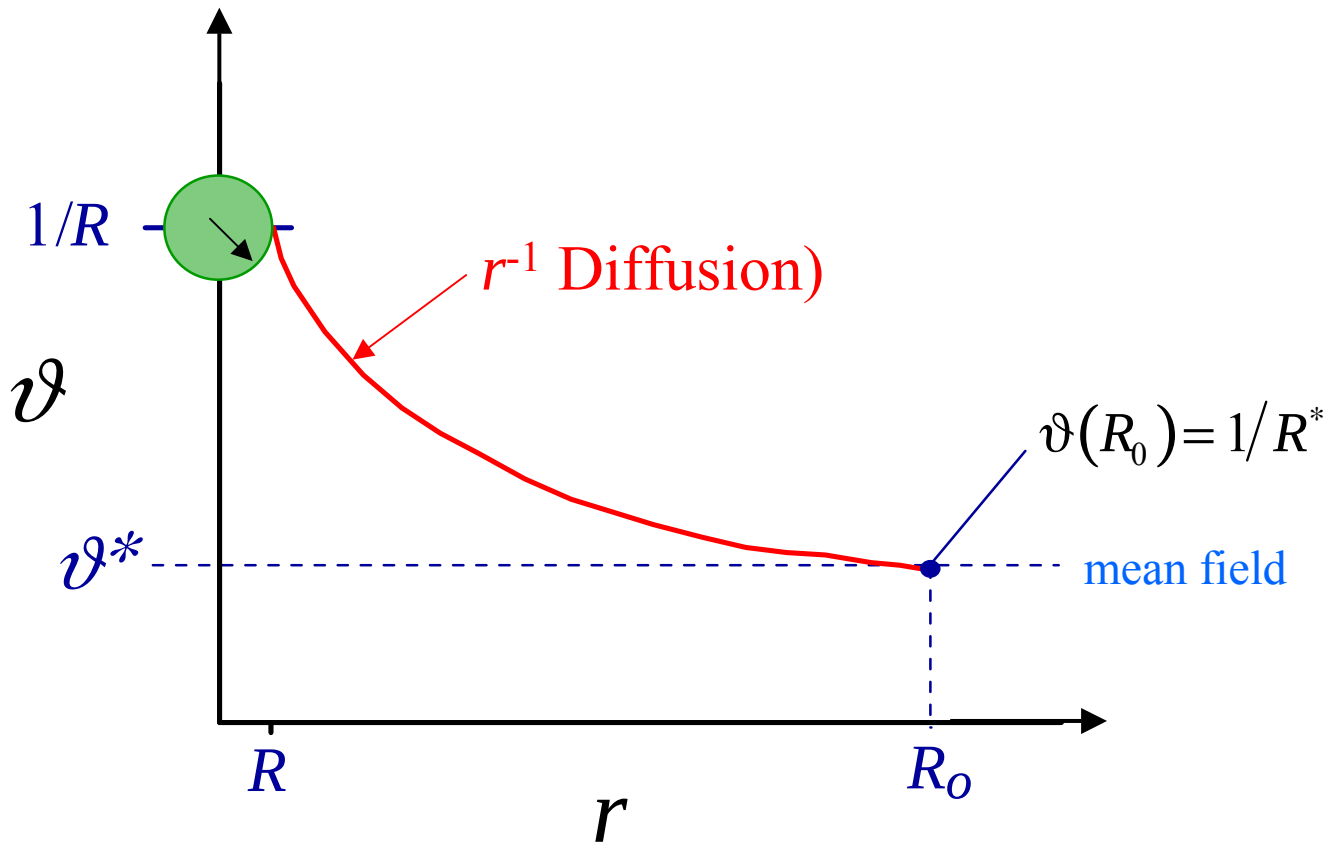
Where R is the droplet radius.

LSW Mean-Field Description



$$B = R^2 \frac{\mathrm{d}R}{\mathrm{d}t} = R^2 \left(\frac{\partial \vartheta}{\partial r}\right)_R = \frac{R}{R^*} - 1$$

LaPlacian Interaction, R_0



$$B = R^2 \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{\rho - 1}{1 - \rho/\rho_0}$$

Where B is the volume flux of material to/from a droplet of radius R, and ρ renormalized droplet radius (R/R^*) where R^* is critical radius in equilibrium with mean field.

Random Field Cell

- Yukawa potential:

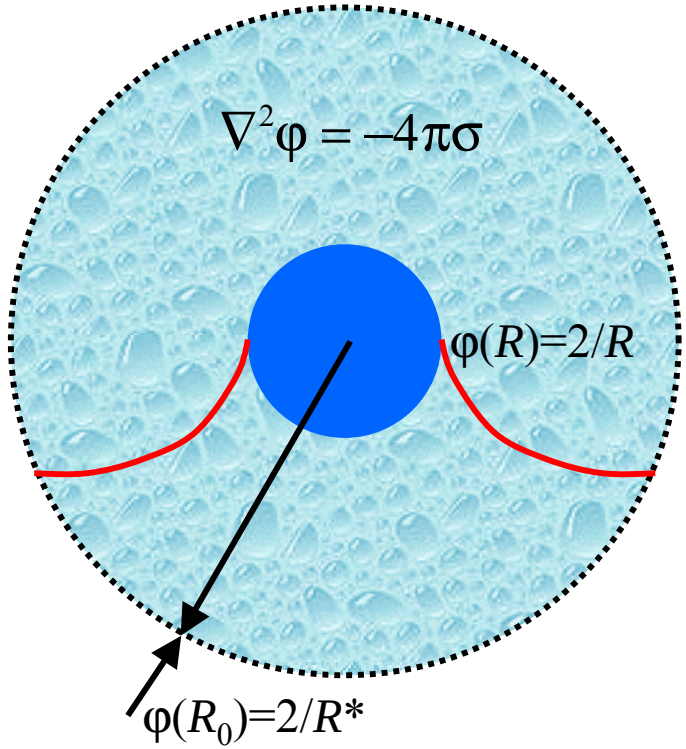
$$\varphi(r) = \frac{2}{R^*} + \frac{B}{R_0} e^{-\kappa R_0} - \frac{B}{r} e^{-\kappa r}$$

- Volume flux:

$$B = \frac{2\left(R - R^*\right)}{R^*\left[e^{-\kappa R} - \frac{R}{R_0} e^{-\kappa R_0}\right]} \cong B_{LSW}(1 + \kappa R)$$

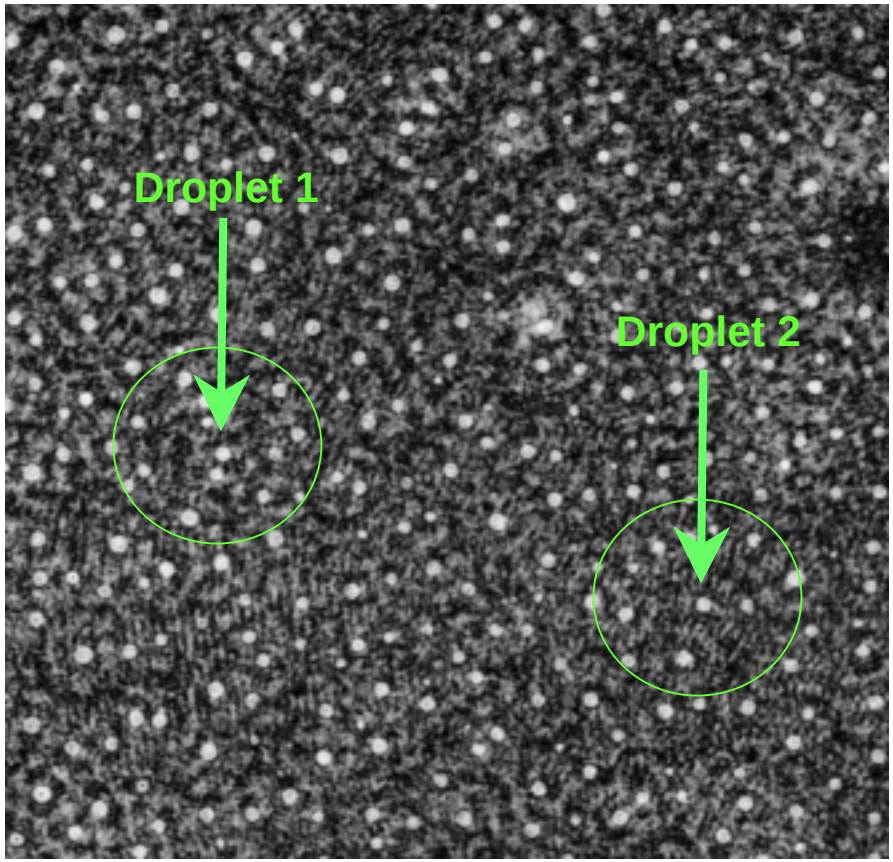
- Screening Length=Cut-off:

$$\kappa \equiv \left(4\pi N_V \langle R \rangle\right)^{\frac{1}{2}} \cong R_0^{-1} = \sqrt{3V_V \frac{\langle R \rangle}{\langle R^3 \rangle}}$$



Where κ is the screening length which introduces interparticle interactions, hence local fields into coarsening dynamics. B_{LSW} is the volume flux for particles not experiencing interparticle interactions. These particles only interact with mean field (LSW: Lifshitz, Slyozov, Wagner). φ is the diffusion potential, σ is the particle source/sink density (for diffusion) and corollary to charge density from Debye-Huckel theory for Coulombic potential. N is the number of particles per unit volume within a cluster, and V_v is the volume fraction of droplets within a given cluster.

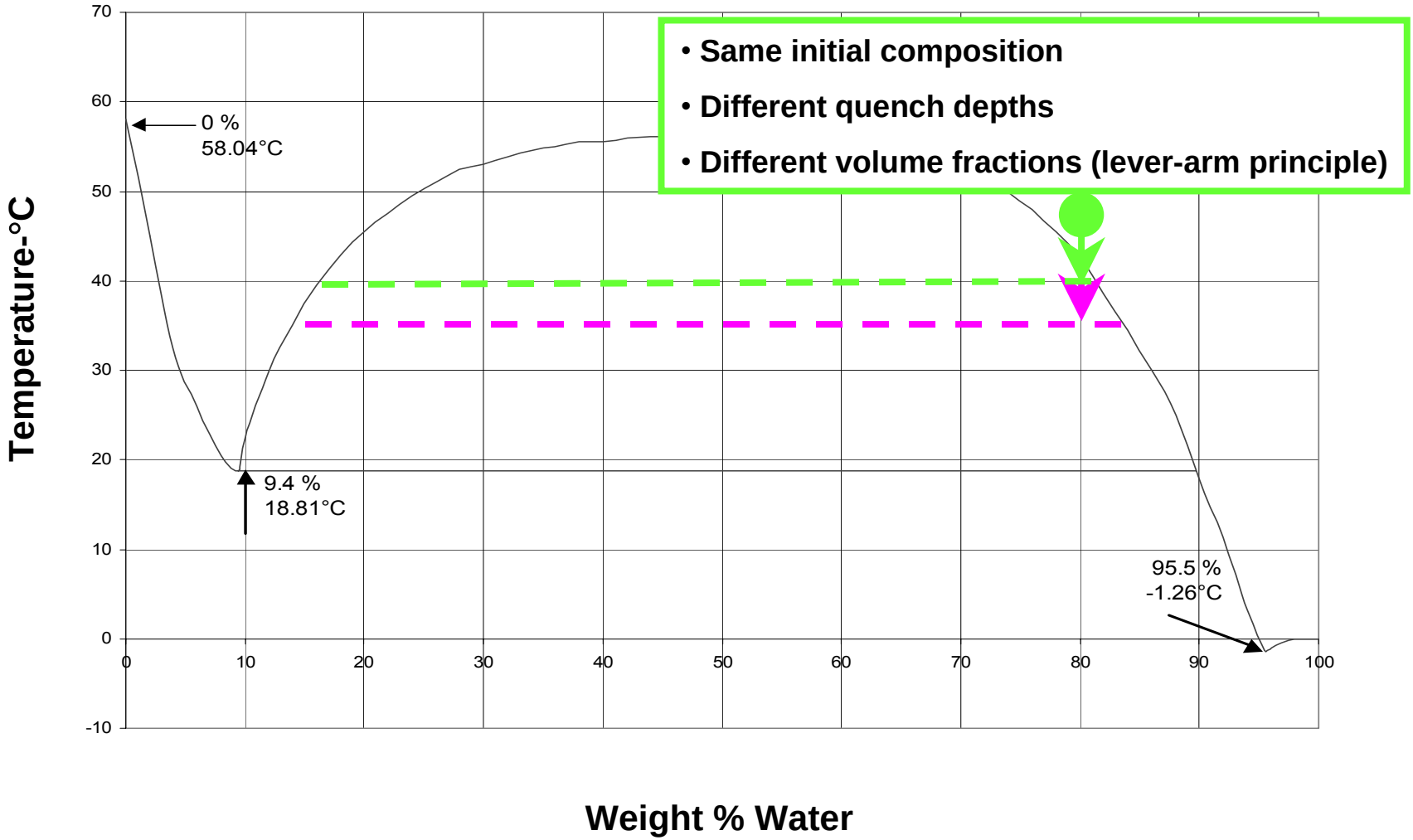
Variation in Spatial Distribution "Locale Noise"

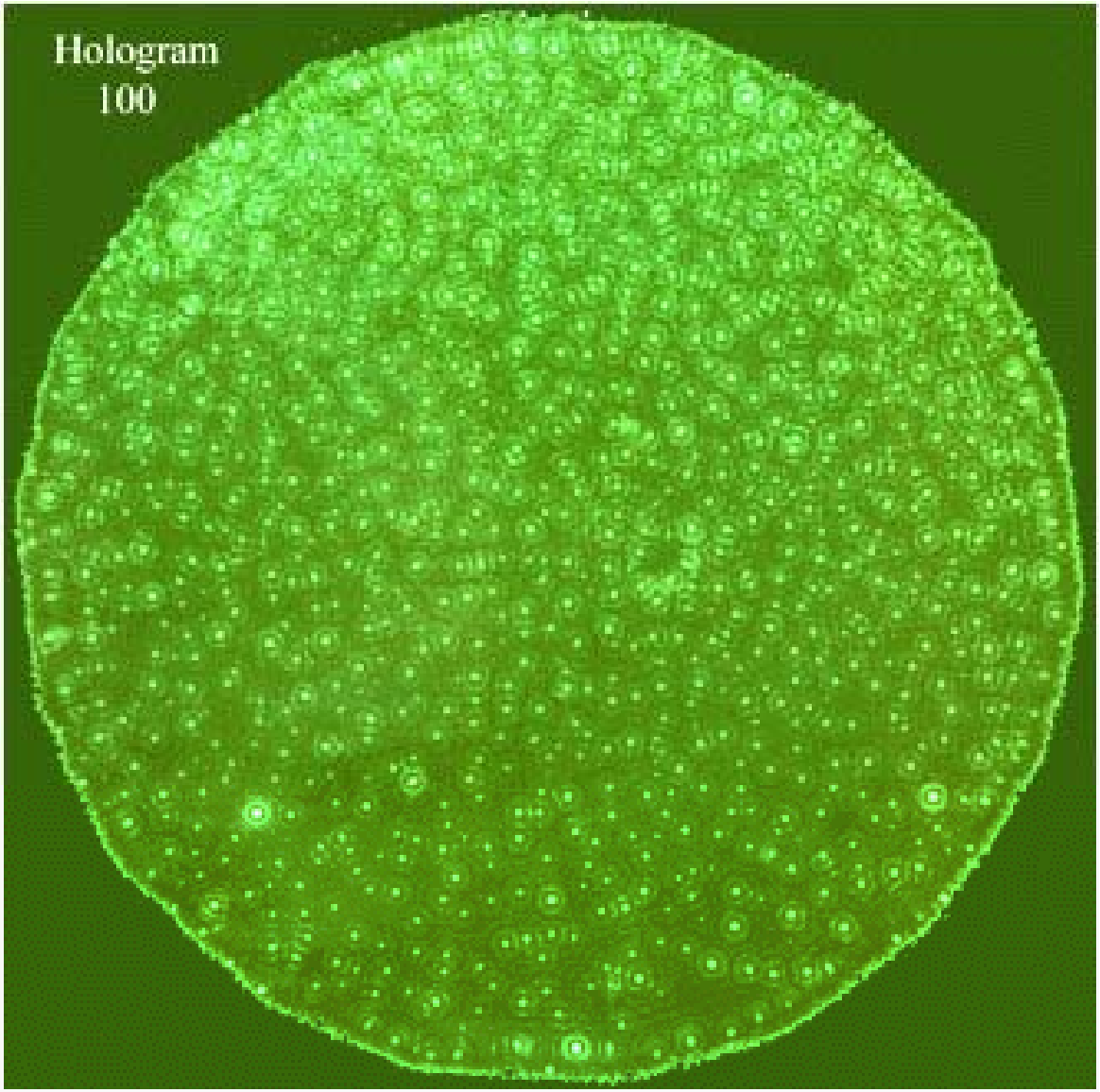


100 mm

Because of variation in droplet distributions within their local environments, Droplets 1 and 2 may not behave as mean field predictions would indicate.

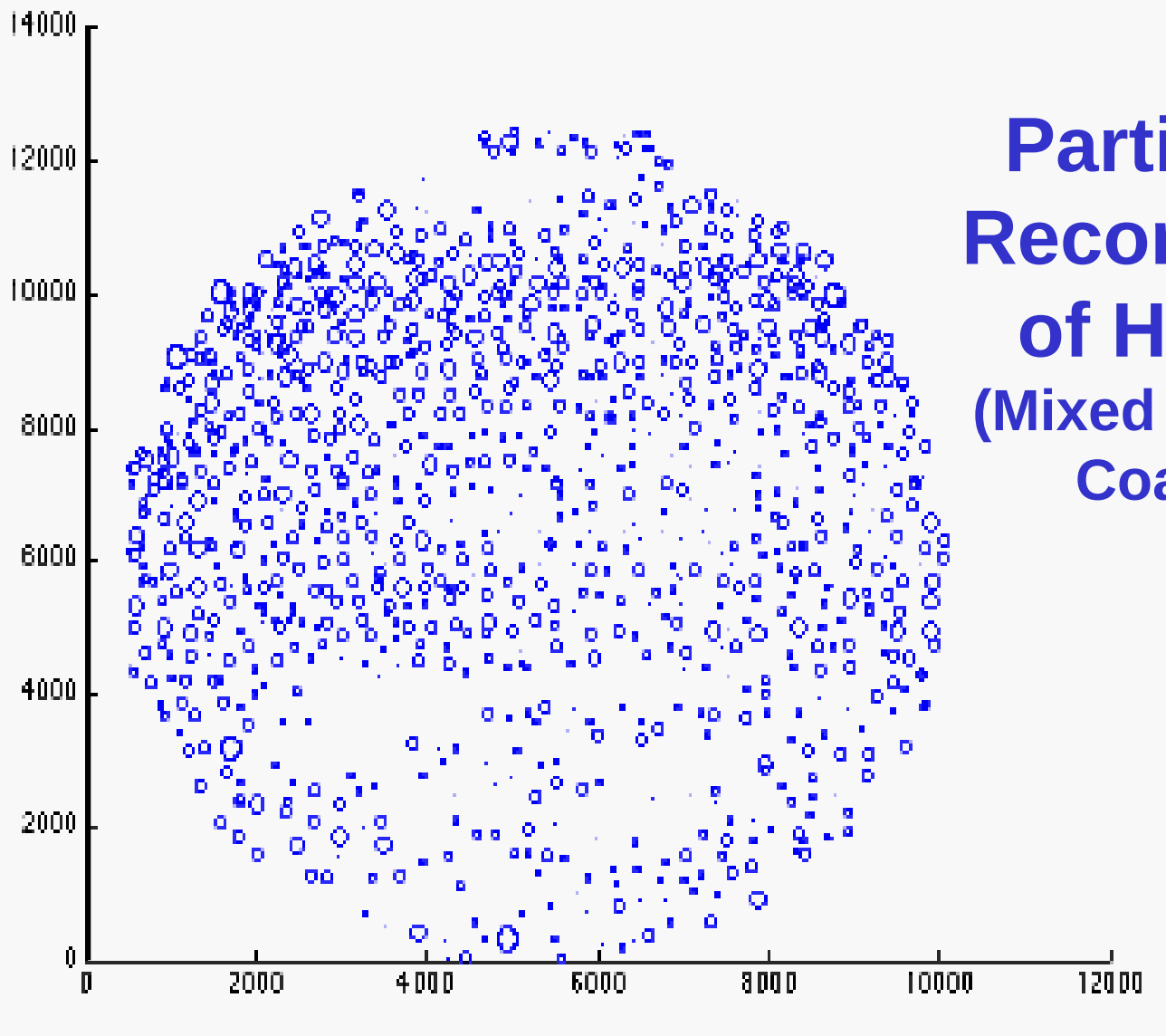
Quench Depth and Volume Fraction





Hologram 100
Mixed Dimensional Coarsening

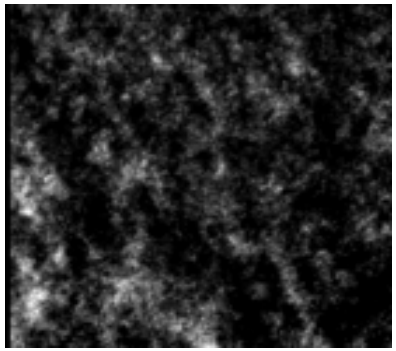
16 mm diameter test cell

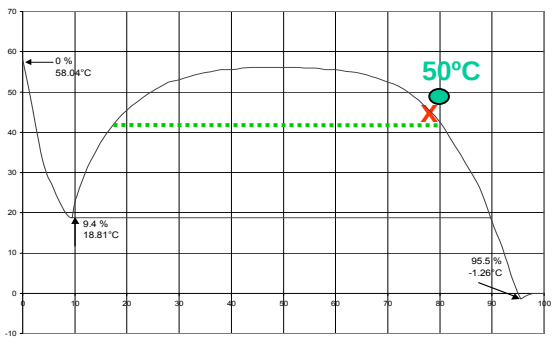


Particle Field Reconstruction of Hologram

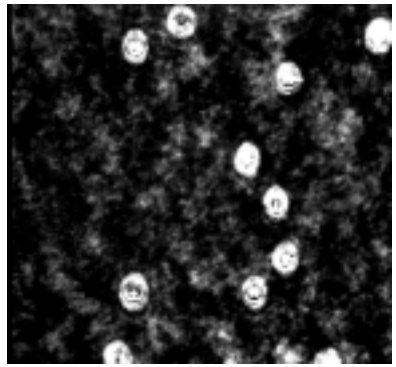
(Mixed Dimensional Coarsening)

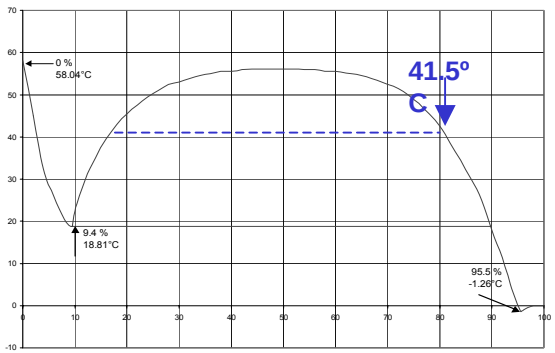
100 mm



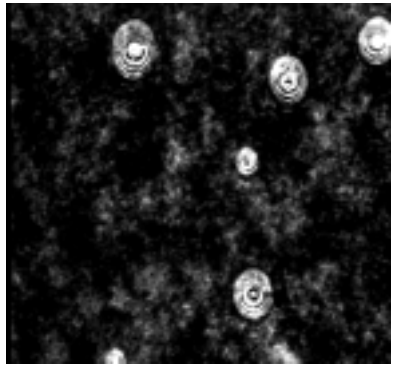


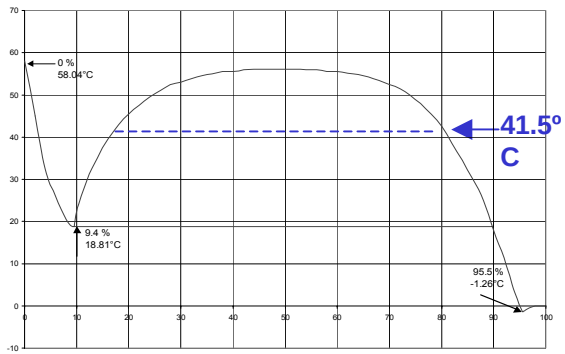
Homogeneous at 50ºC





After quench to 41.5 ºC





After extended isothermal soak

x **Indicates the bulk composition of the sample**

Spaceflight Holography Investigation in a Virtual Apparatus (SHIVA)

William K. Witherow

The movement of a particle in a fluid is one of the most fundamental processes in physics and plays an important role in materials science. For example, the physics of crystal growth from a nucleation site in solution can be dominated by movement of the solution over the crystal surface. Gravity usually dominates the equations of motion, but in microgravity other terms can dominate, making the equation much more complex. Until recently, the equations were solved only by numerical methods and/or by neglecting terms. During this study, we discovered an exact solution to the equations, which shows that the usually neglected terms become extremely important in microgravity. We also developed diagnostic recording methods using holography to save all of the particle field data, allowing the experiment to essentially be transferred from space back to earth in what we call the "virtual apparatus". We will record holograms of particle distributions in motion in microgravity and bring them back to earth for analysis, allowing the study of the full three-dimensional motion of sets of particles, allowing us to test the new analytical solutions. The experiment will also provide accurate measurements of the quasi-steady acceleration of the space platform and other interesting microgravity and g-jitter effects. This program will produce the flight definition for an experiment in the microgravity environment of space to validate the theoretical model. We will design an experiment with the help of the theoretical model that is optimized for testing the model, measuring g, g-jitter, and other microgravity phenomena.

Spaceflight Holography Investigation in a Virtual Apparatus (SHIVA)

- PI - Dr. J. Trolinger – Metrolaser Incorporated
- Co-I – Roger Rangel – University of California in Irvine
- Carlos Corimba – University of Hawaii, Manoa
- Ravindra B. Lal – A & M University
- Jan Rogers and William Witherow – MSFC

- Project Scientist – David Smith
- Project Manager – Melanie Bodiford
- Systems Engineer – William Patterson

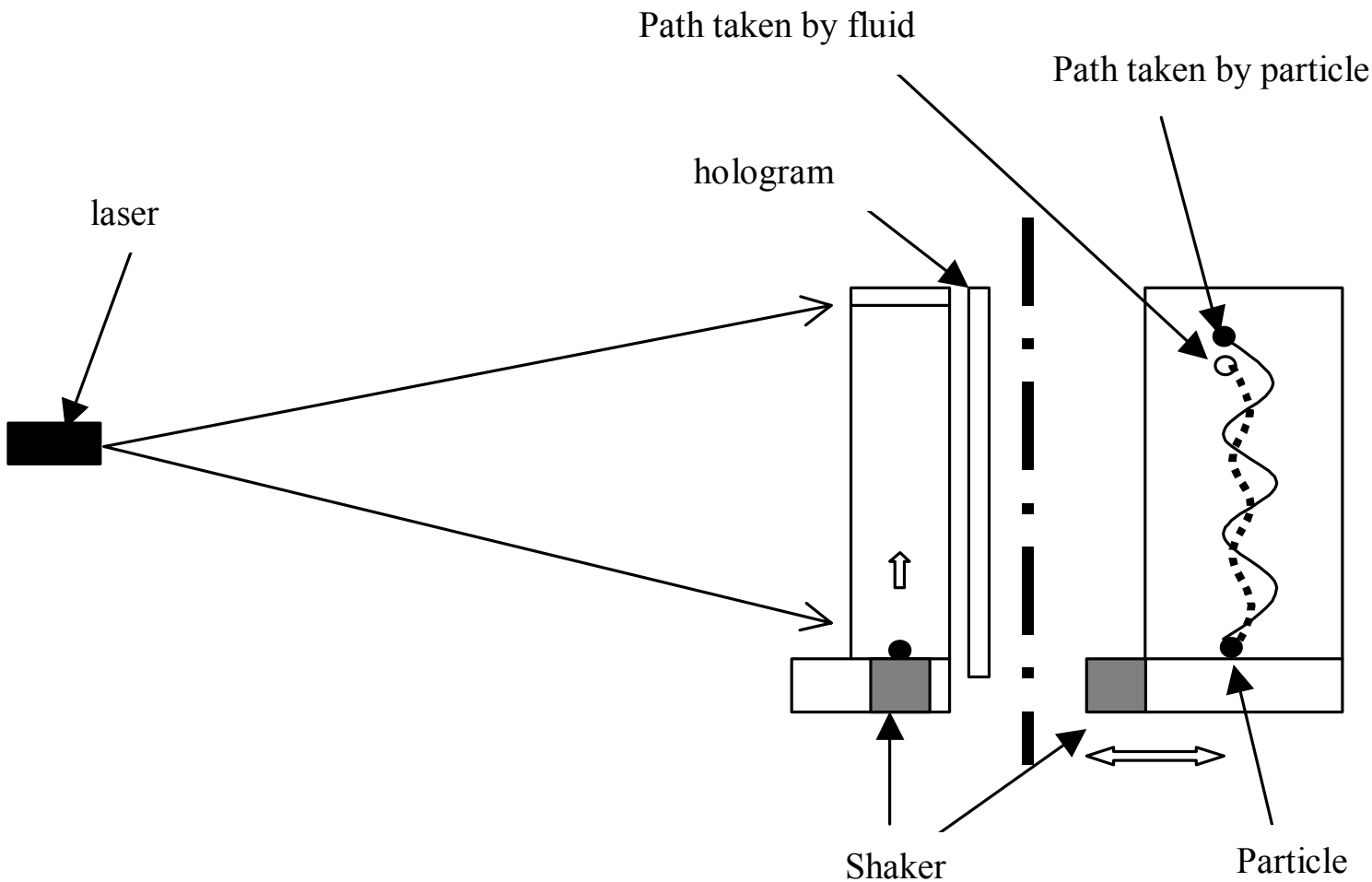
Team Members

- Ron Young Pace&Waite/SD44
- Abrams, Russ MSFC/ED12
- Alexander, Jane MSFC/ED17
- Beabout, Brent MSFC/ED12
- Beabout, Dyana MSFC/ED12
- Bender, Bob Sverdrup/Qualis/ED25
- Bernier, Sonja MSFC/QS30
- Bodiford, Melanie MSFC/SD44
- Chisler, Keith CST
- Coimbra, Carlos University of Hawaii
- Funkhouser, Glenn Morgan Research/FD36
- Gooch,Glen Sverdrup/ED35
- Hamilton, George MSFC/ED42
- Jennings, John MSFC/ED21
- Kappus, Kathy MSFC/ED27
- Karigan, Michael MSFC/ED23
- Lackey, Jeff MSFC/ED24
- Lal, Ravi Alabama A&M
- Miernik, Janie ERC/Sverdrup /ED24
- Mitchell, Karen MSFC/ED24
- Mitchell, Michael MSFC/ED35
- Patterson, Bill Pace&Waite/SD42
- Pendergrass, T. K. SD43
- Phillips, Edward
- Pope, Regina ERC/Sverdrup/ED21
- Qualis/Sverdrup/ED24
- Rabun, Phyllis Sverdrup/ED24
- Rangel, Roger University of California/Irvine
- Rasberry, Tonia HEI/Quality
- Rogers, Dr. Jan MSFC/SD46
- Smith, Dr. David MSFC/SD46
- Spurgeon, Jennifer HEI/SQ22
- Trolinger, Dr. Jim Metrolaser
- Waggoner, Jason MSFC/ED24
- Witherow, Bill MSFC/SD46

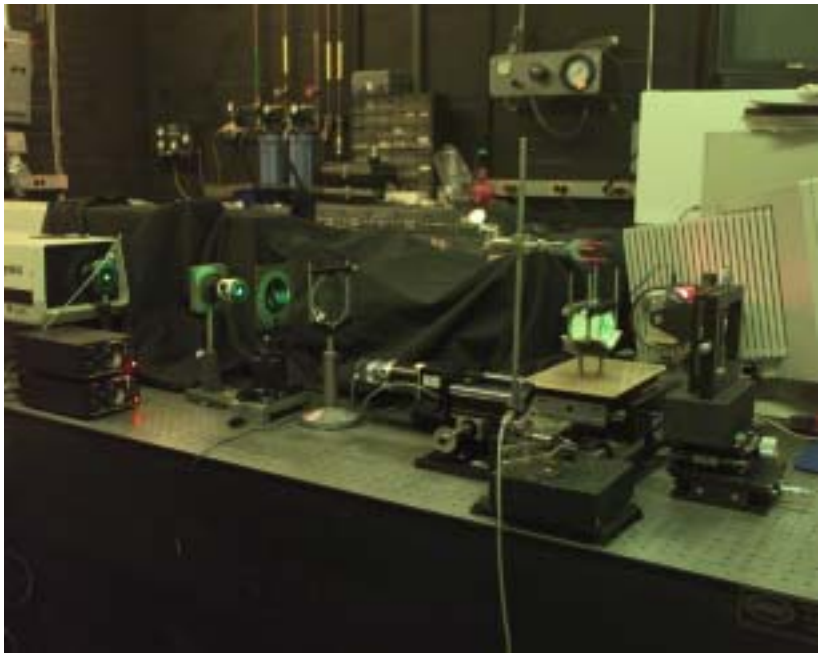
Milestones

- **Science Concept Review (SCR) – successfully completed September 6, 2000**
- **Requirements Definition Review (RDR) scheduled for 2004**
- **Holographic Film Test – currently ongoing**
- **Breadboard layout – testing has begun**

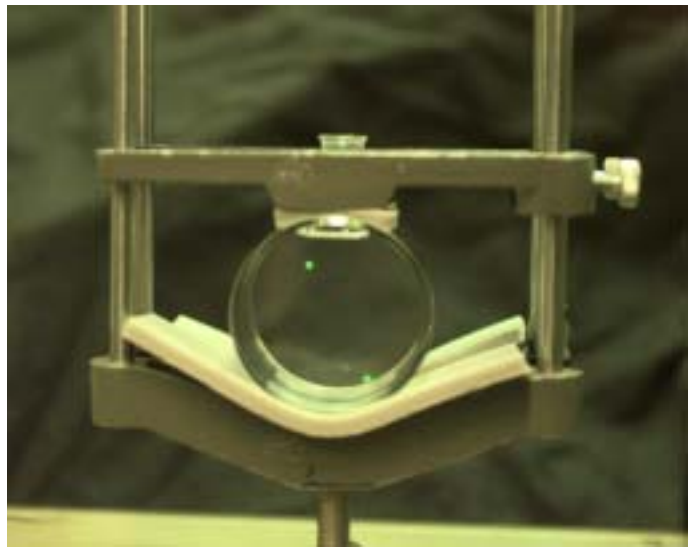
SHIVA Ground Experiment



Translation Table Experiment

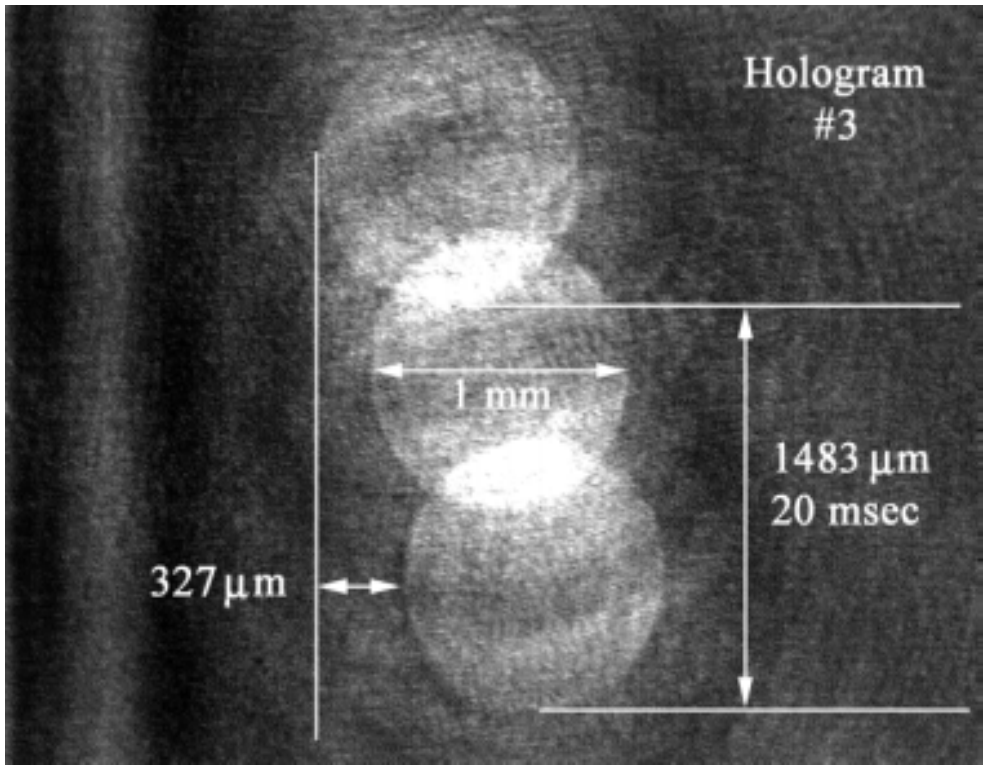


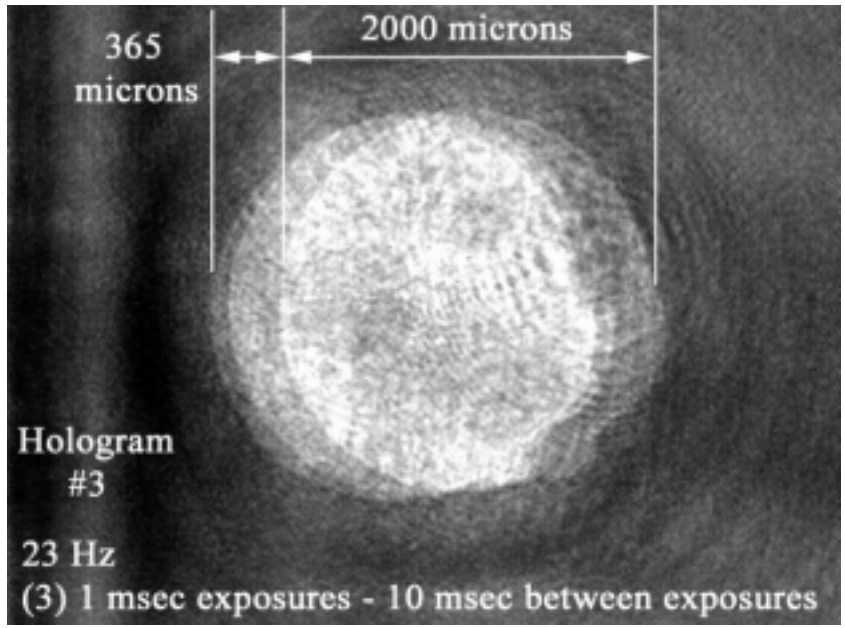
Optics and Translation Table



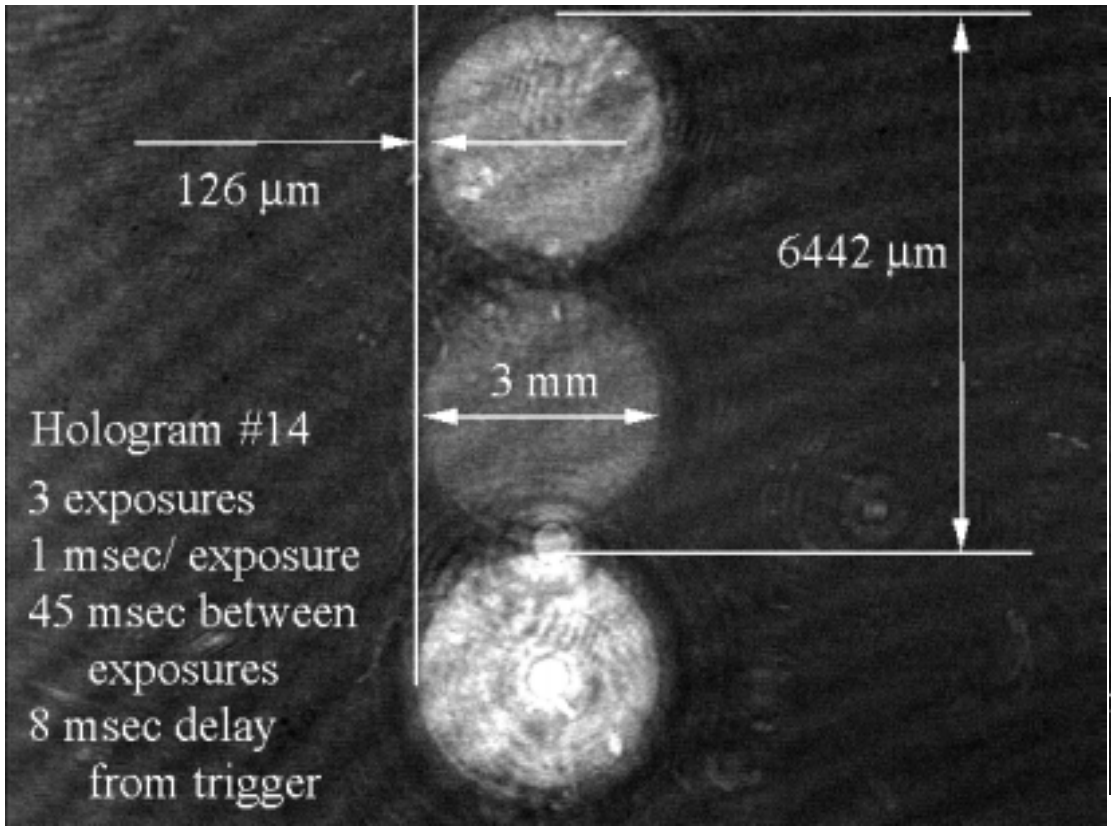
Test Cell

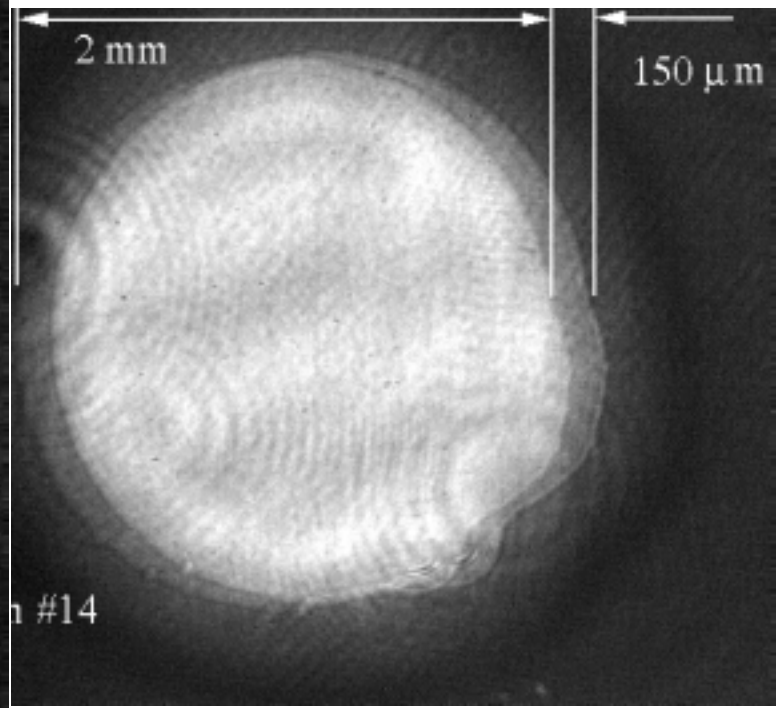
Steel Sphere in Krytox



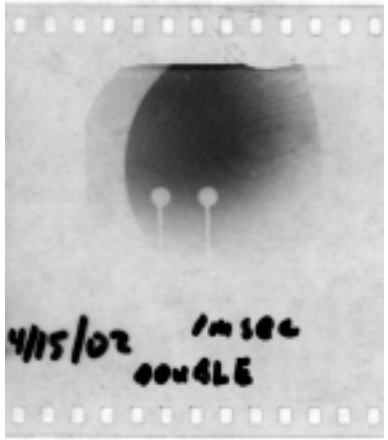


Ceramic Sphere in Krytox





Film Exposure Tests



Primary View - Room Lights Off

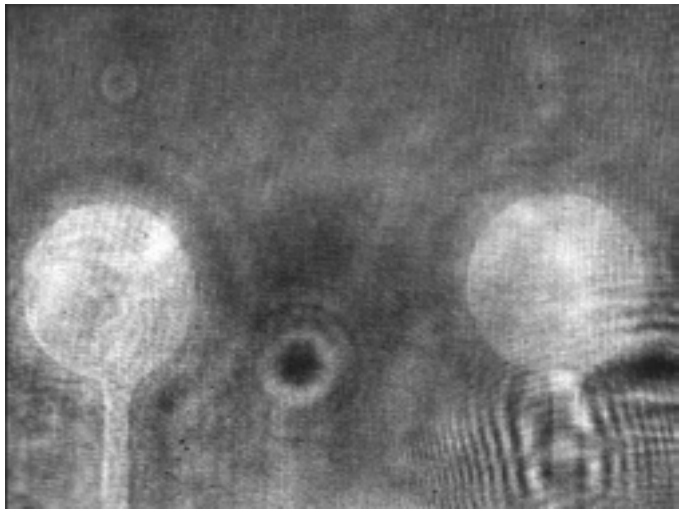
Primary View - Room Lights On

Secondary View - Room Lights Off

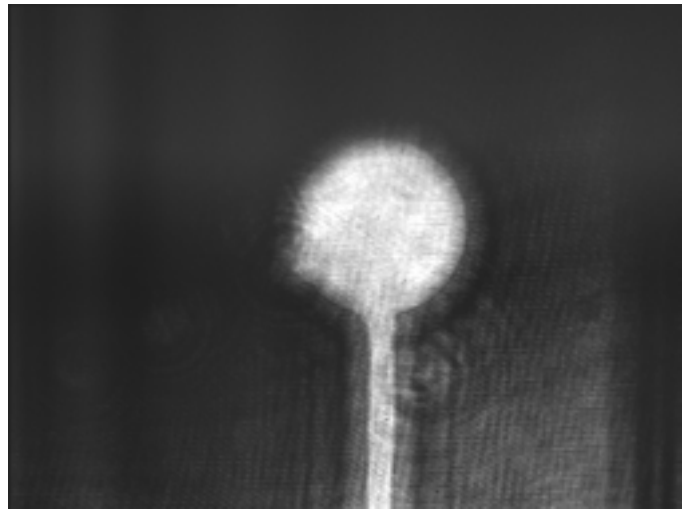
Secondary View - Room Lights On

Reconstructed Holograms from Breadboard

Primary Path with beam shearer

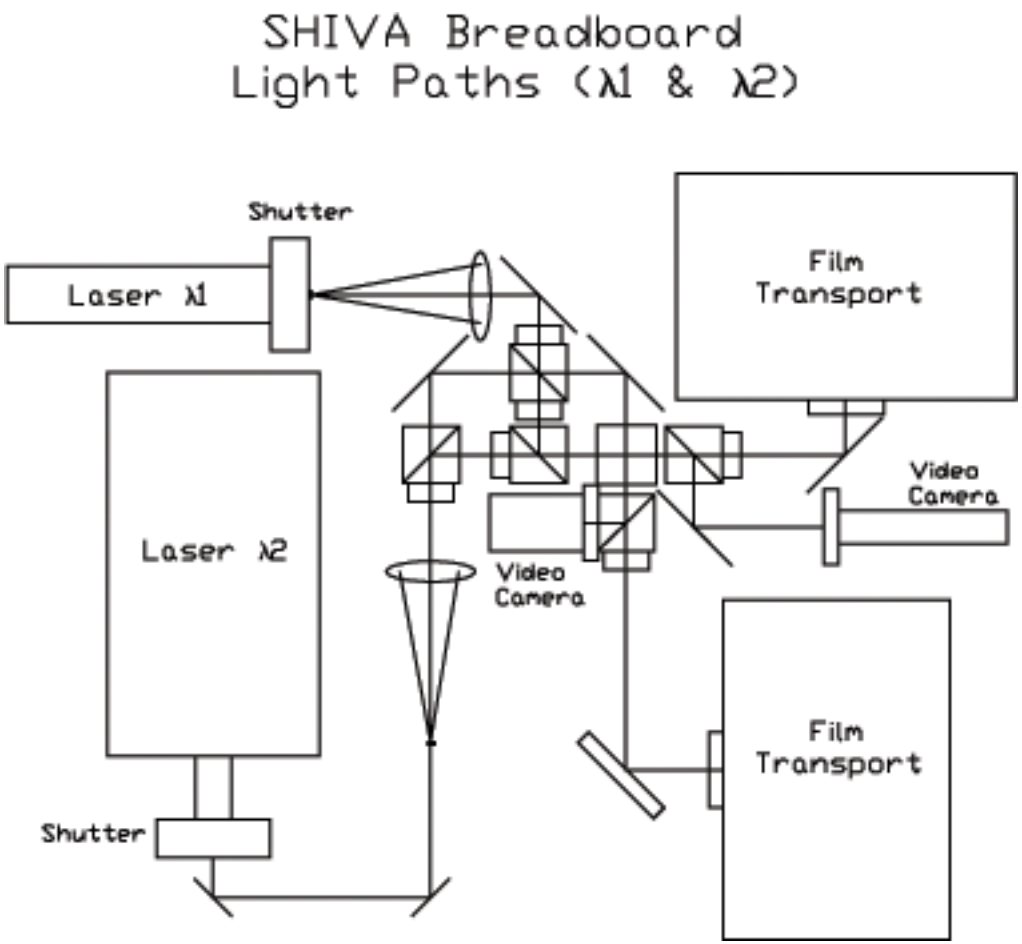


Secondary Path

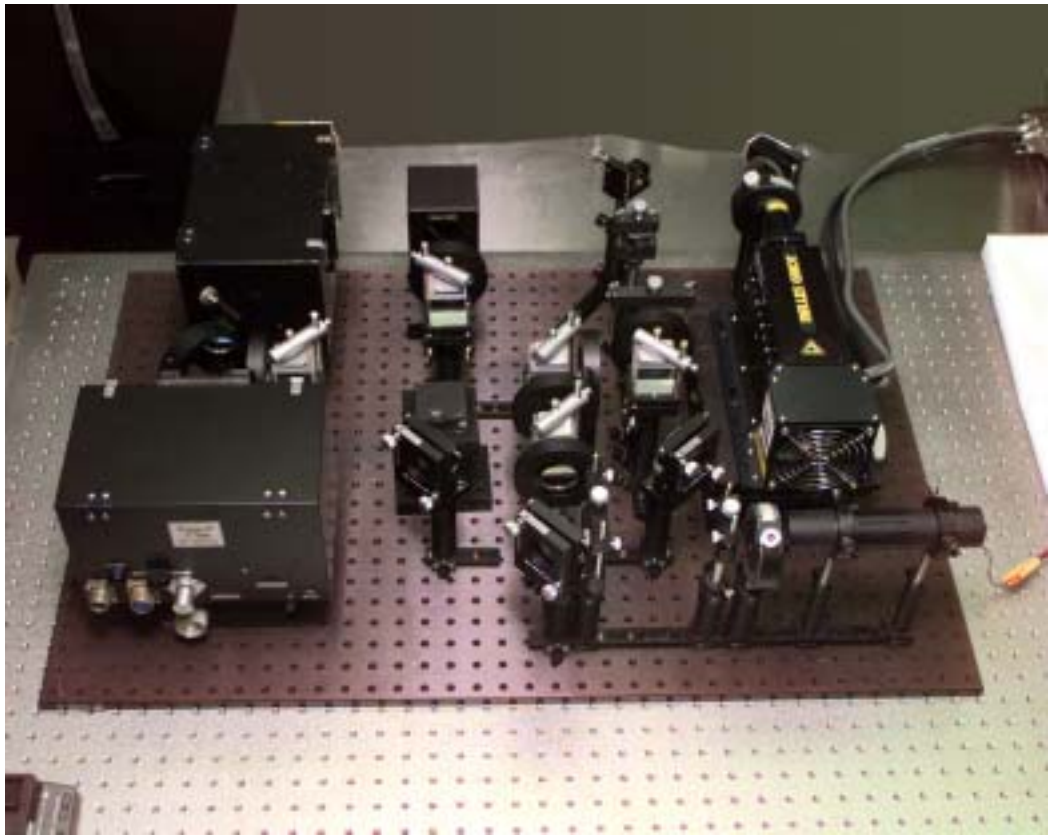


Images are of a 2 mm diameter steel sphere mounted on a 275 micron diameter fiber. The two images from the primary path are due to the beam shearer that is in that path.

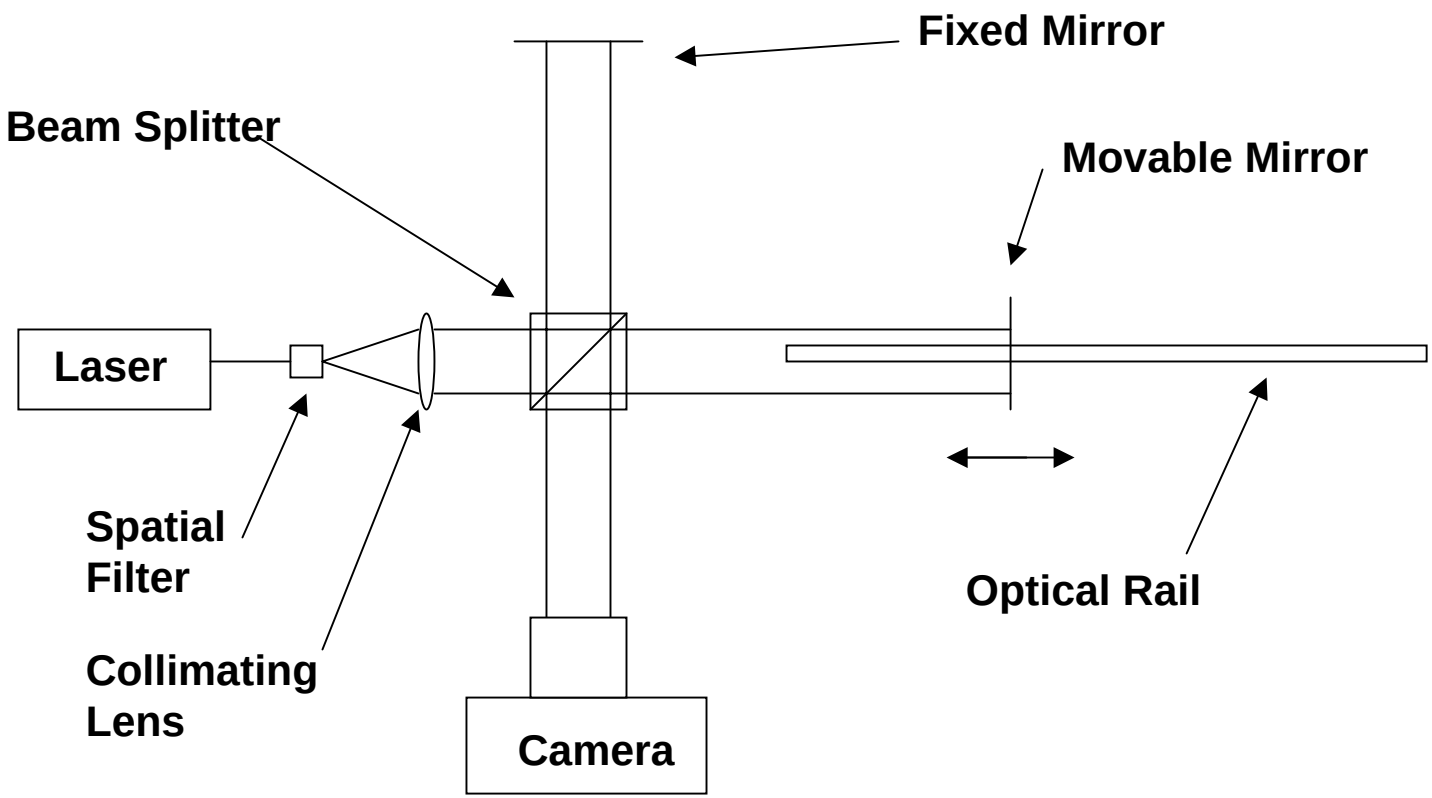
Optics Schematic



Breadboard System

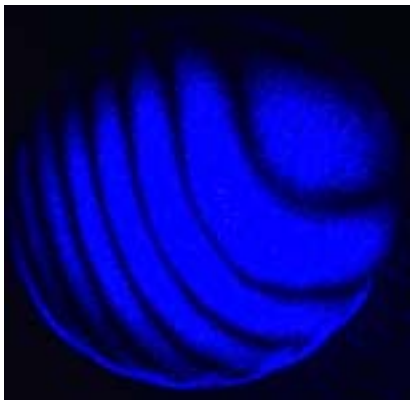


Laser Coherence Test



Michelson Interferometer

Coherence Test



Pathlength difference between mirrors – 0 cm

Pathlength difference between mirrors – 16 cm

Particle Engulfment and Pushing by Solidifying Interfaces (PEP)

D.M. Stefanescu (PI)[1], S. Sen[2], A.V. Catalina[2], F.R. Juretzko[1], P.A. Curreri[3]

[1] The University of Alabama, Tuscaloosa, AL 35487

[2] University Space Research Association, Huntsville, AL 35806

[3] NASA Marshall Space Flight Center, Huntsville, AL 35812

Abstract

The study of particle behavior at solid/liquid interfaces (SLI's) is at the center of the *Particle Engulfment and Pushing* (PEP) research program. Interactions of particles with SLI's have been of interest since the 1960's, starting with geological observations, i.e., frost heaving. Ever since, this field of research has become significant to such diverse areas as metal matrix composite materials, fabrication of superconductors, and inclusion control in steels. The PEP research effort is geared towards understanding the fundamental physics of the interaction between particles and a planar SLI. Experimental work including 1-g and μ-g experiments accompany the development of analytical and numerical models.

The experimental work comprised of substantial groundwork with aluminum and zinc matrices containing spherical zirconia particles, μ-g experiments with metallic Al matrices and the use of transparent organic metal-analogue materials. The modeling efforts have grown from the initial steady-state analytical model to dynamic models, accounting for the initial acceleration of a particle at rest by an advancing SLI. To gain a more comprehensive understanding, numerical models were developed to account for the influence of the thermal and solutal field. Current efforts are geared towards coupling the diffusive 2-D front tracking model with a fluid flow model to account for differences in the physics of interaction between 1-g and μ-g environments. A significant amount of this theoretical investigation has been and is being performed by co-investigators at NASA MSFC

The impetus of the first μ-g experiment (LMS, 1996) with metallic matrices was the proof of concept and technical feasibility. The second μ-g experiments (USMP-4, 1997) with organic materials yielded a substantial database for the evaluation of PEP theoretical models. For the LMS mission pre and post processing characterization of metallic samples, including distribution of zirconia particles, were carried out at MSFC using the unique X-ray Transmission Microscope. For the USMP-4 glovebox experiment, design of hardware and proof of concept experiments on parabolic flights was carried out by co-investigators at MSFC.

Current efforts are geared towards the development of suitable ampoules for planned experiments on board the International Space Station (ISS), in conjunction with verification of the thermal requirements of the Quench Module Insert (QMI) furnace module. MSFC is supporting the PI in developing a validated furnace thermal model to assist him in his ampoule design and currently tests are being performed to evaluate the performance of the ISS furnace insert.

PARTICLE ENGULFMENT AND PUSHING BY SOLIDIFYING INTERFACES (PEP)

SCIENCE TEAM

D. M. Stefanescu (PI, UA, Tuscaloosa), S. Sen (USRA/MSFC), A. V. Catalina (USRA/MSFC), F.R. Juretzko (UA), and P.A. Curreri (NASA MSFC)

PROJECT MANAGER

Monica Hammond

PROJECT SCIENTIST

Subhayu Sen

SYSTEM ENGINEER

Richard Hagood

FURNACE & SACA TEAM

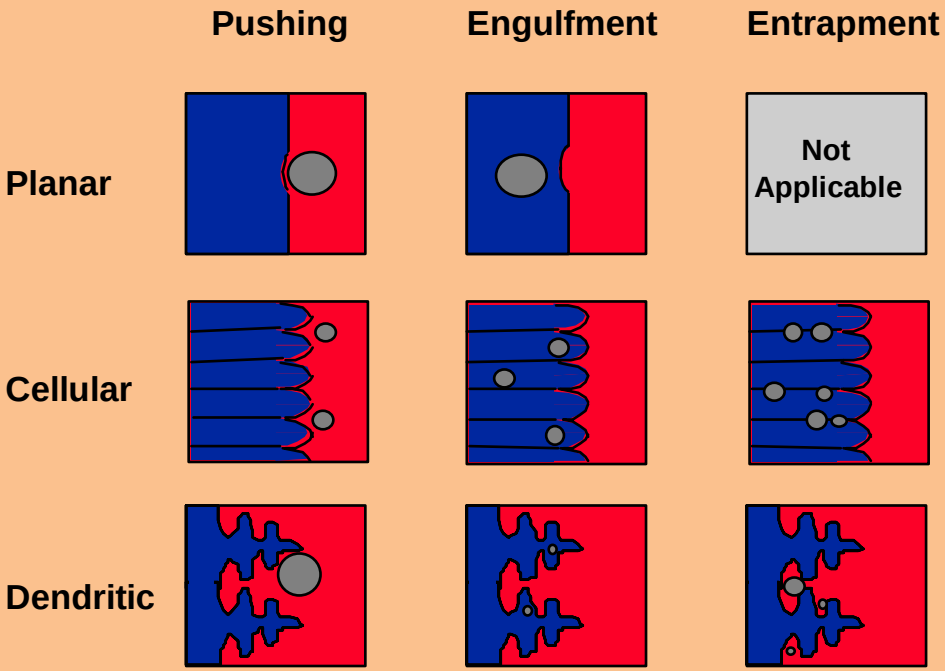
Barry Battista, Jenny Bellomy-Ezell, Deborah Hernandez,

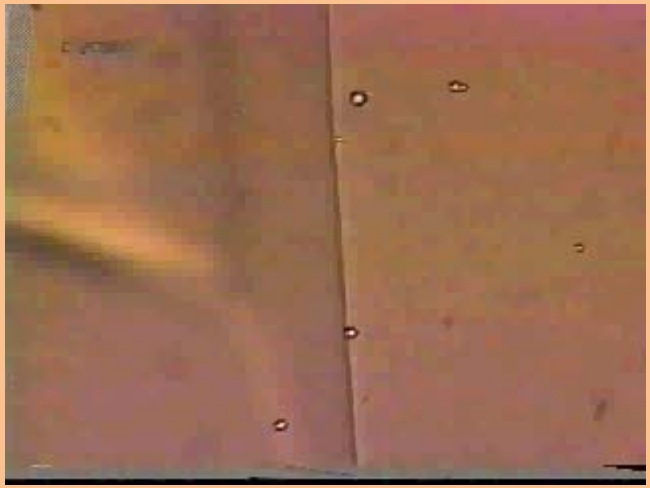
Norris Vaughn, Julia Khodabandeh, Shawn Breeding

Acknowledgements

- NASA Office of Physical & Biological Research
- Prof. W. Kaukler
- Dr. A. Bune
- Dr. P. Peters
- Drs. D. Gillies & S. Cobb

Science



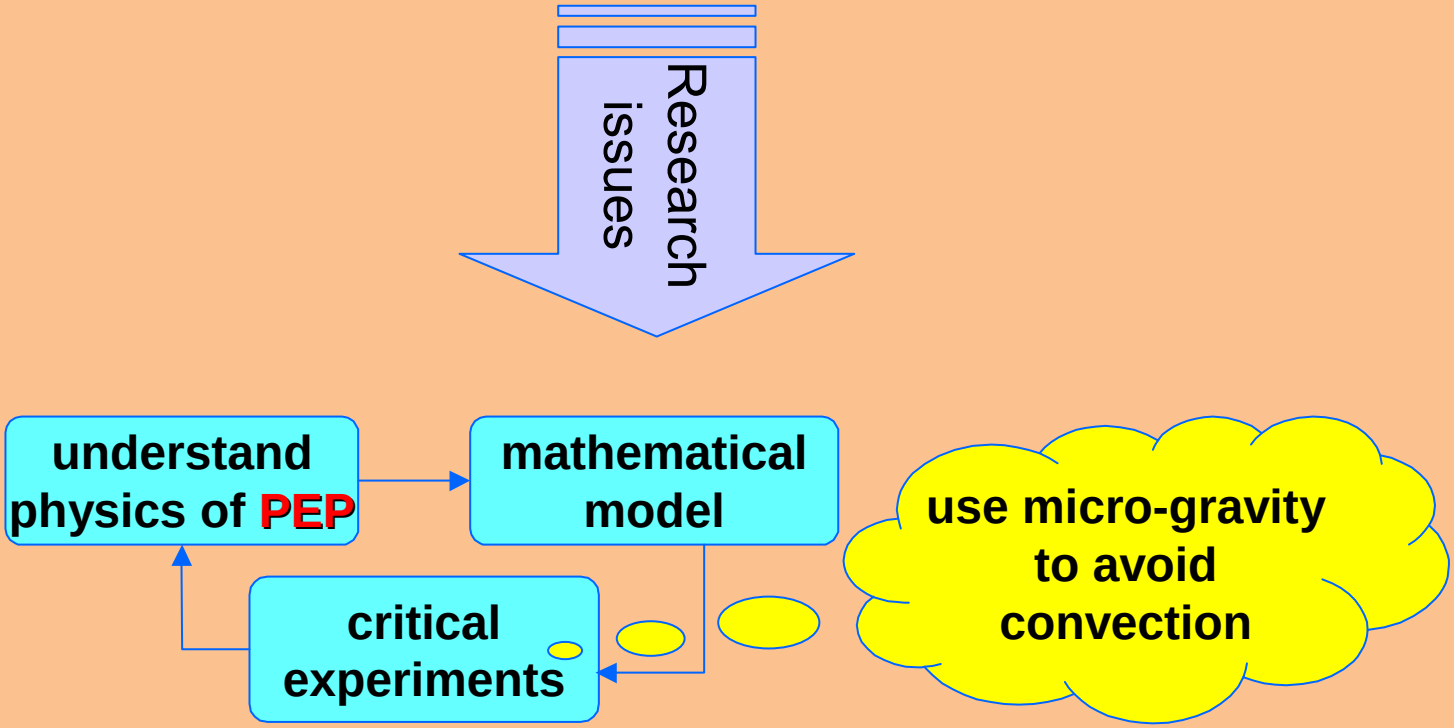


possible scenarios in different alloy systems

OBJECTIVES

$$V_{CR} \propto \frac{1}{R_p}$$

Where V_{cr} is the critical velocity and R_p is the particle radius.



Impact on Industry

"All domestic cars must achieve a 27.5 mile per gallon corporate average fuel economy (CAFE)."
US Congress

solution

Replace cast iron/steel components with metal matrix composites (MMC)

PEP contribution

PEP *addresses the issue of uniform distribution of particles in MMCs for higher strength and low density components*

Incorporation of inclusions in steel ingots and castings has a detrimental effect on mechanical properties

solution

Predict and control inclusion distribution

PEP contribution

Theoretical models developed for **PEP** *have been used to predict distribution of such inclusion in commercial steel*
Shibata, et. al, ISIJ International, 38 (1998), sponsored by Kawasaki Steel

Application of high T_c superconductors suffers from inability to carry high current.

solution

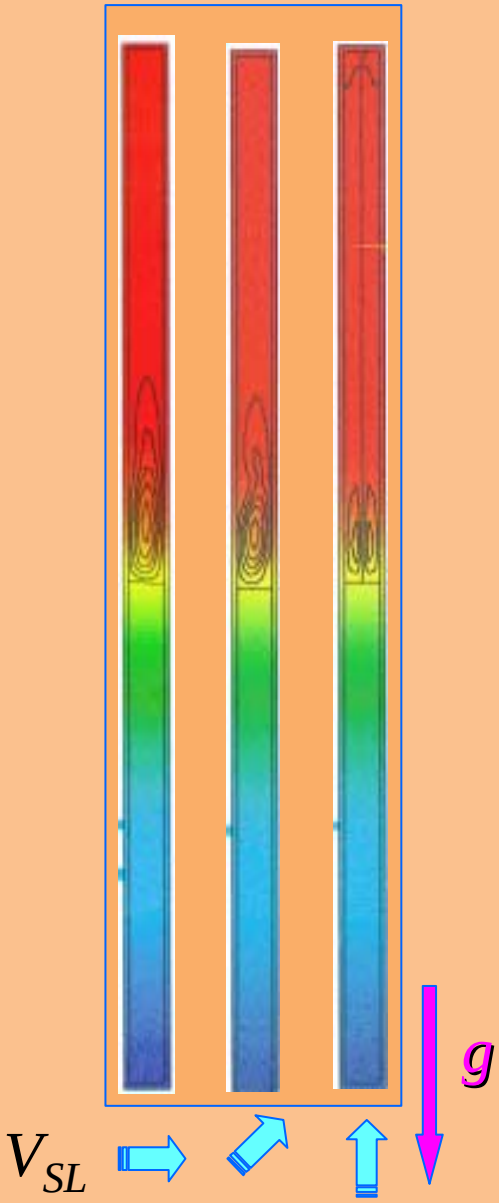
Precipitation of flux pinning uniformly distributed $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_{7-\delta}$ matrix.

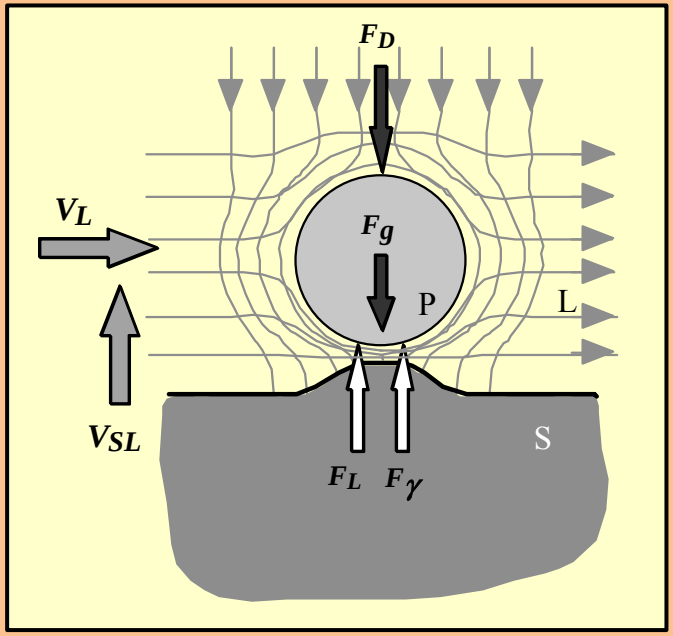
PEP contribution

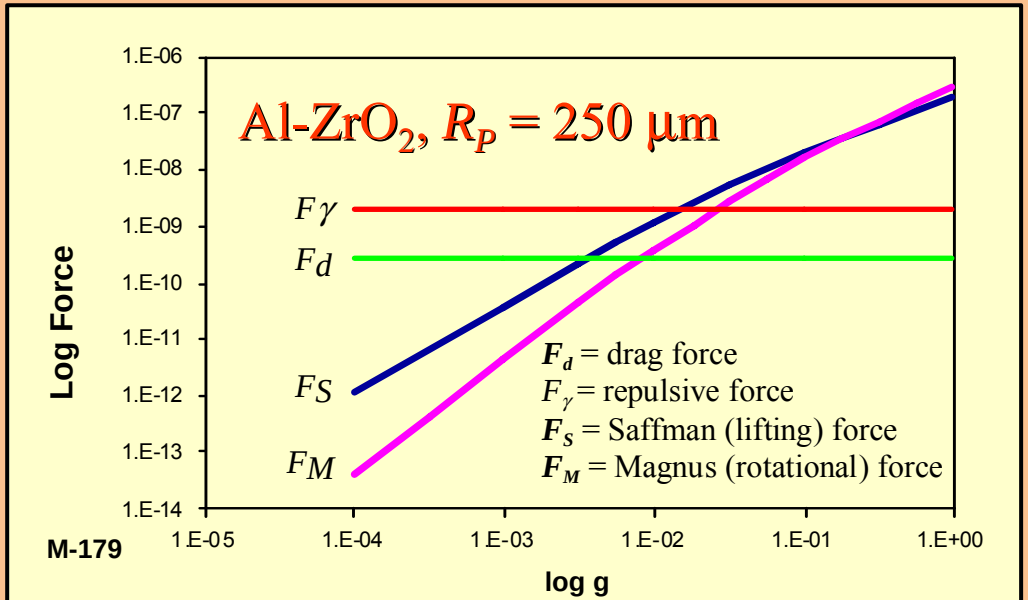
Theoretical models developed for **PEP** *have been used to predict distribution of $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_{7-\delta}$ matrix*
Endo et. al, Physica C, 273 (1996)

Justification For Micro-g

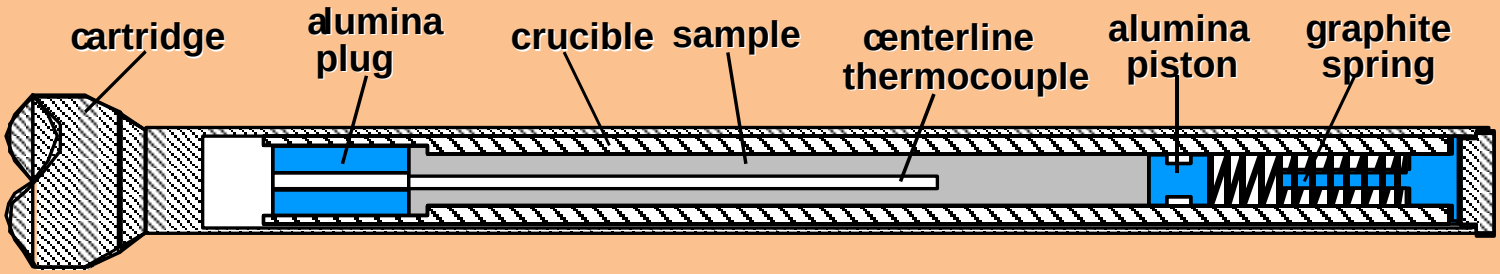
- Bune and Sen (MSFC)



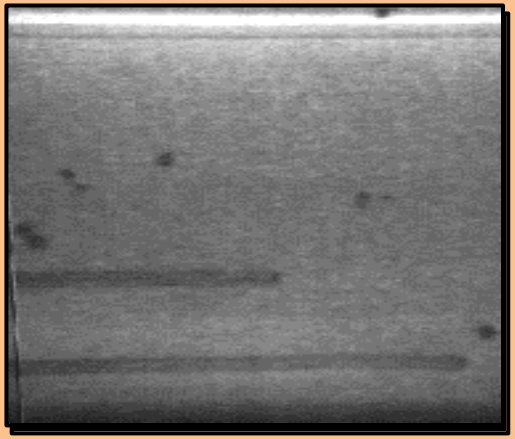




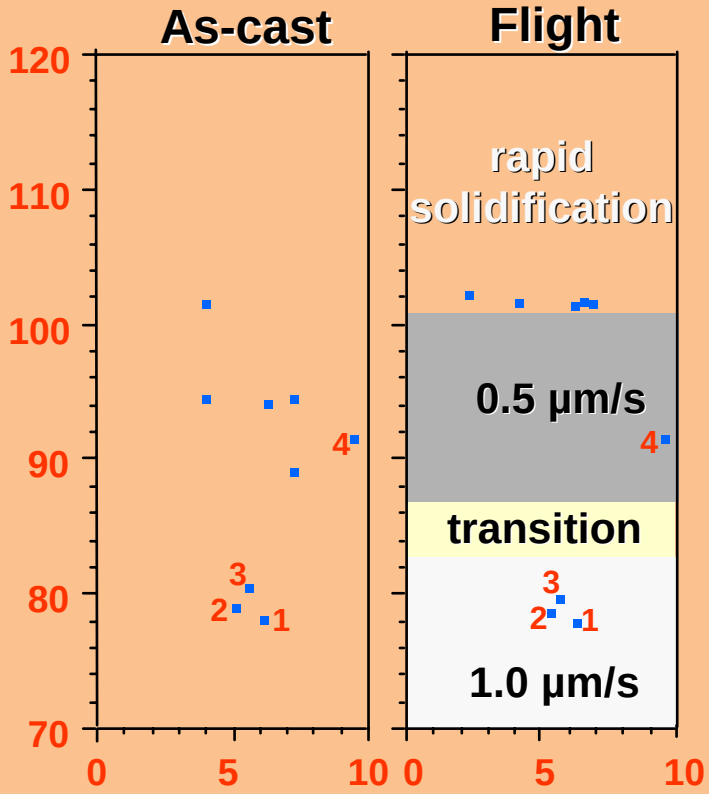
LMS MISSION, 1996



Kaukler (MSFC) and Sen (MSFC)



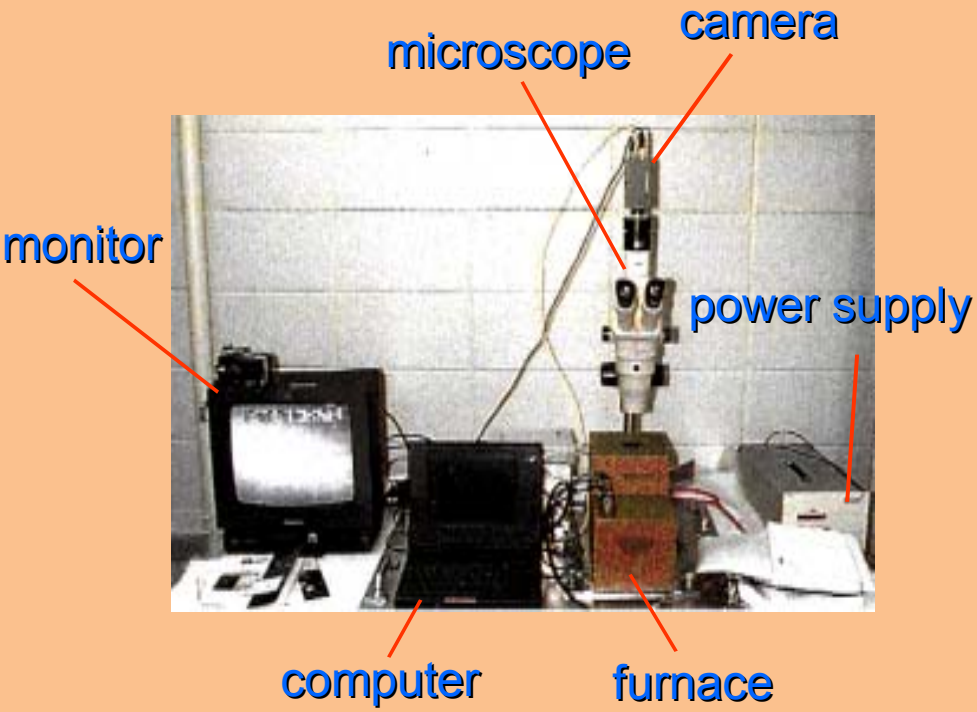
XTM analysis of sample pre- and post-processing, ZrO_2 (R = 250 µm) in pure Al

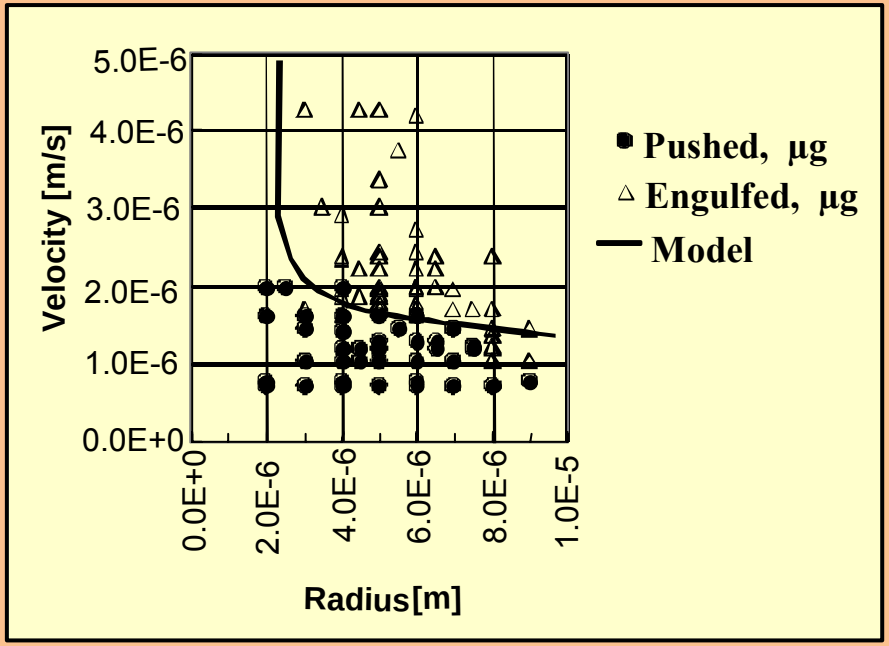


V_{CR} (earth) = 1.9 - 2.4 µm/s

V_{CR} (µg) = 0.5 - 1.0 µm/s

USMP-4 MISSION,1997





SCN with polystyrene particles

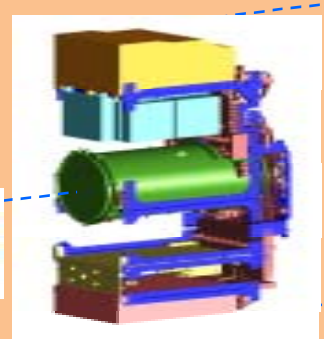
Future Plans ?

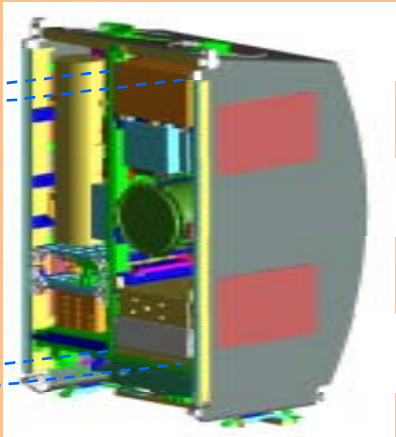
Sample Ampoule or Crucible

Sample Ampoule Cartridge Assembly

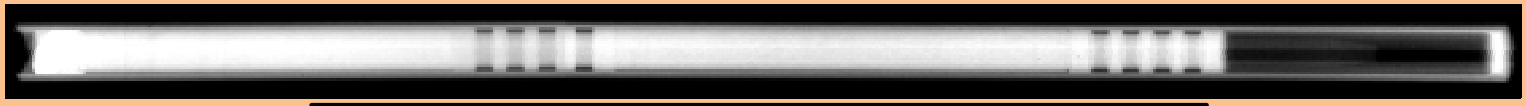
Insert(s)
- QMI
- DMI
- LGF
- SQF
- FMF

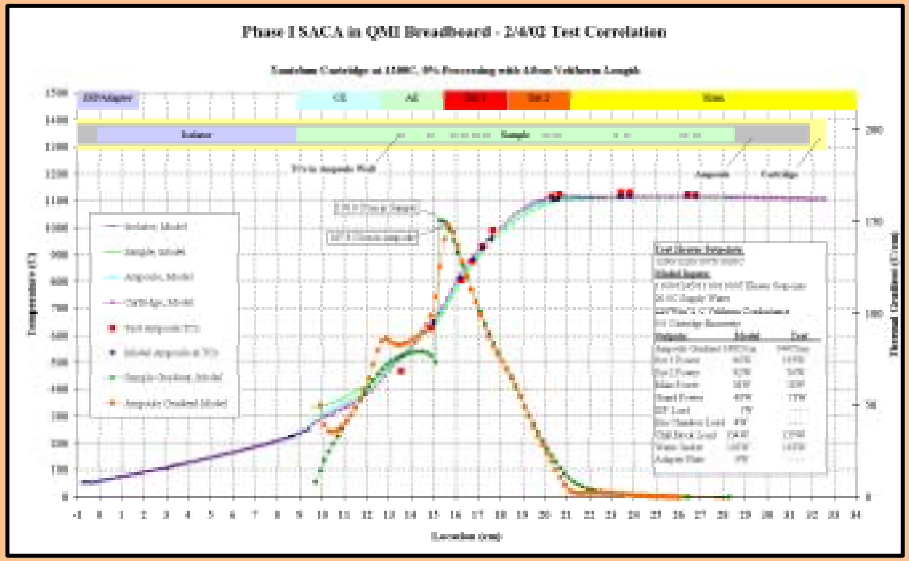
Experiment Module





Ampoule Design & BB Testing
ED 22 (NASA MSFC) and TMI





SUMMARY

- **Science Support at MSFC**
  - Theoretical model development
  - Ground based real-time experiments using XTM
  - Non-destructive (XTM) characterization of ground and flight samples
- **Engineering Support at MSFC**
  - Thermal model development for PI specific ampoule design
  - Ampoule fabrication and QMI breadboard testing

Numerical modeling and fluids experiments for materials processing and protein crystallization.

N. Ramachandran, USRA

The presentation will highlight two of the three NASA funded projects I am working on, namely:

1.Principal Investigator: Study of Fluid Flow Control in Protein Crystallization Using Strong Magnetic Fields. CoIs: F. Leslie and E. Ciszak - Fluid physics NRA

2.Co Investigator: Fundamental Studies of Crystal Growth of Microporous Materials, Flight definition research grant *with* Dr. Prabir Dutta, PI, The Ohio State University

3.Co Investigator: Crystal Growth of ZnSe and related Ternary Compound Semiconductors by Vapor Transport *with* Dr. Ching-Hua Su, PI, NASA MSFC

The following is a brief outline of the protein crystallization project.

I*ntroduction*

An important component in biotechnology, particularly in the area of protein engineering and rational drug design is the knowledge of the precise three-dimensional molecular structure of proteins. The quality of structural information obtained from X-ray diffraction methods is directly dependent on the degree of perfection of the protein crystals. As a consequence, the growth of high quality macromolecular crystals for diffraction analyses has been the central focus for biochemists, biologists, and bioengineers.

Macromolecular crystals are obtained from solutions that contain the crystallizing species in equilibrium with higher aggregates, ions, precipitants, other possible phases of the protein, foreign particles, the walls of the container, and a likely host of other impurities. By changing transport modes in general, i.e., reduction of convection and sedimentation, as is achieved in “microgravity”, we have been able to dramatically affect the movement and distribution of macromolecules in the fluid, and thus their transport, formation of crystal nuclei, and adsorption to the crystal surface. While a limited number of high quality crystals from space flights have been obtained, as the recent National Research Council (NRC) review of the NASA microgravity crystallization program pointed out, the scientific approach and research in crystallization of proteins has been mainly empirical yielding inconclusive results [1].

Hypothesis

We postulate that we can reduce convection in ground-based experiments and we can understand the different aspects of convection control through the use of strong magnetic fields and field gradients. We postulate that limited convection in a magnetic field will provide the environment for the growth of high quality crystals. The approach exploits the variation of fluid magnetic susceptibility with concentration for this purpose and the convective damping is realized by appropriately positioning the crystal growth cell so that the magnetic susceptibility force counteracts terrestrial gravity.

Objective

The general objective is to test the hypothesis of convective control using a strong magnetic field and magnetic field gradient and to understand the nature of the various forces that come into play. Specifically we aim to delineate causative factors and to quantify them through experiments, analysis and numerical modeling. Once the basic understanding is obtained, the study will focus on testing the hypothesis on proteins of pyruvate dehydrogenase complex (PDC), proteins E1 and E3. Obtaining high crystal quality of these proteins is of great importance to structural biologists since their structures need to be determined. Our approach will simultaneously provide the first implementation of our flow control hypotheses and investigation described in this proposal.

Specific goals for the investigation are:

1. To develop an understanding of convection control in diamagnetic fluids with concentration gradients through experimentation and numerical modeling. Specifically solutal buoyancy driven convection due to crystal growth will be considered.
2. To develop predictive measures for successful crystallization in a magnetic field using analyses and numerical modeling for use in future protein crystal growth experiments. This will establish criteria that can be used to estimate the efficacy of magnetic field flow damping on crystallization of candidate proteins.
3. To demonstrate the understanding of convection damping by high magnetic fields to a class of proteins that is of interest and whose structure is as yet not determined.
4. To compare quantitatively, the quality of the grown crystals with and without a magnetic field. X-ray diffraction techniques will be used for the comparative studies.

Value

The proposed work is ground-based with both theoretical and experimental investigation of crystallization phenomena with emphasis on the important fluid physics element of the protein crystallization process. Further, the proposed investigation employs an interdisciplinary approach to advance the research in the important area of biocrystallization and thus biotechnology. Understanding the fluid flow due to solutal buoyancy convection and controlling that flow through the application of a strong magnetic field and field gradient are important objectives. This implies obtaining quantitative information through carefully conducted experiments, developing predictive capability through analytical and numerical simulations, and applying it to proteins whose structures are as yet undetermined. The studies will directly provide a predictive tool and a technique to further reduce convective contamination in Space experiments onboard the ISS.

Our research will determine whether the use of a strong magnetic field has significant impact on the crystallization of the most challenging macromolecular systems. Extending our success in crystallization in a magnetic field with proteins from arguably the most exciting and challenging multienzyme assembly of the human body, i.e. pyruvate dehydrogenase complex will certainly provide a breakthrough for macromolecular crystal growers.

1. National Research Council, Space Studies Board, Commission on Physical Sciences, Mathematics and Applications, in Future Biotechnology Research on the International Space Station, national Academy Press, Washington, DC., 2000, 10-16.

Ongoing Projects

N. Ramachandran, USRA

- ***Principal Investigator:*** **Study of Fluid Flow Control in Protein Crystallization Using Strong Magnetic Fields. Cols: F. Leslie and E. Ciszak - Fluid physics NRA**
- ***Co Investigator:*** **Fundamental Studies of Crystal Growth of Microporous Materials, Flight definition research grant *with* Dr. Prabir Dutta, PI, The Ohio State University**
- ***Co Investigator:*** **Crystal Growth of ZnSe and related Ternary Compound Semiconductors by Vapor Transport *with* Dr. Ching-Hua Su, PI, NASA MSFC**

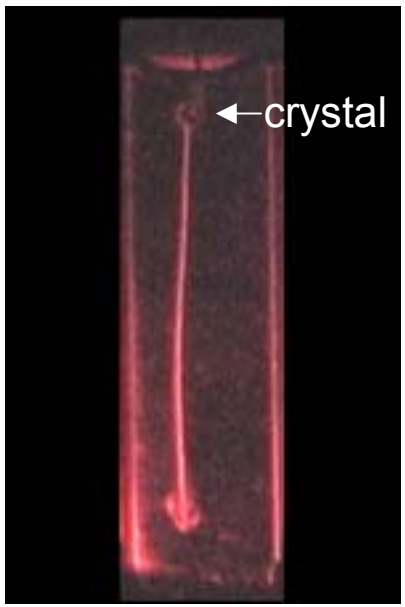
Study of Fluid Flow Control in Protein Crystallization Using Strong Magnetic Fields

Narayanan Ramachandran , Universities Space Research Association

The role of convection in protein crystallization is not clear. This project will use strong magnetic fields to control convection to further understand the phenomena

Why:

- Does convection affect protein crystal growth ? If so, how ?
- Space experiments have yielded inconclusive results with ~ 20% of flight-grown proteins showing promising results
- Can we terrestrially control convection and study the effects ? Can strong magnetic fields provide a terrestrial model for the microgravity environment ?



Schlieren image of solute plume from a dissolving diamagnetic Alum crystal (top) mounted on a sting shows flow augmentation (~16%) by a magnetic force assisting gravity. Experiment done using the 5 Tesla magnet at MSFC

How:

- Use a strong magnetic field and field gradient to control convection in protein crystallization
- Perform carefully controlled protein crystal growth experiments to unambiguously resolve the role of fluid flow in the process
- Develop a rigorous theoretical analysis and numerical model for the technique
- Apply the gained information to grow proteins of high relevance

Impact:

- Prove that the ambiguities of space protein growth experiments can be resolved by ground-based studies
- If convection is not the cause then point to other effects that cause the observed inconsistent growth

> "The prior ambiguous results in space flight experiments in efforts at protein crystallization should be clarified. This experimental investigation using magnetic fields to cancel gravity could be a ground-based method to clarify what happens in microgravity." ATP Letter, October 2001

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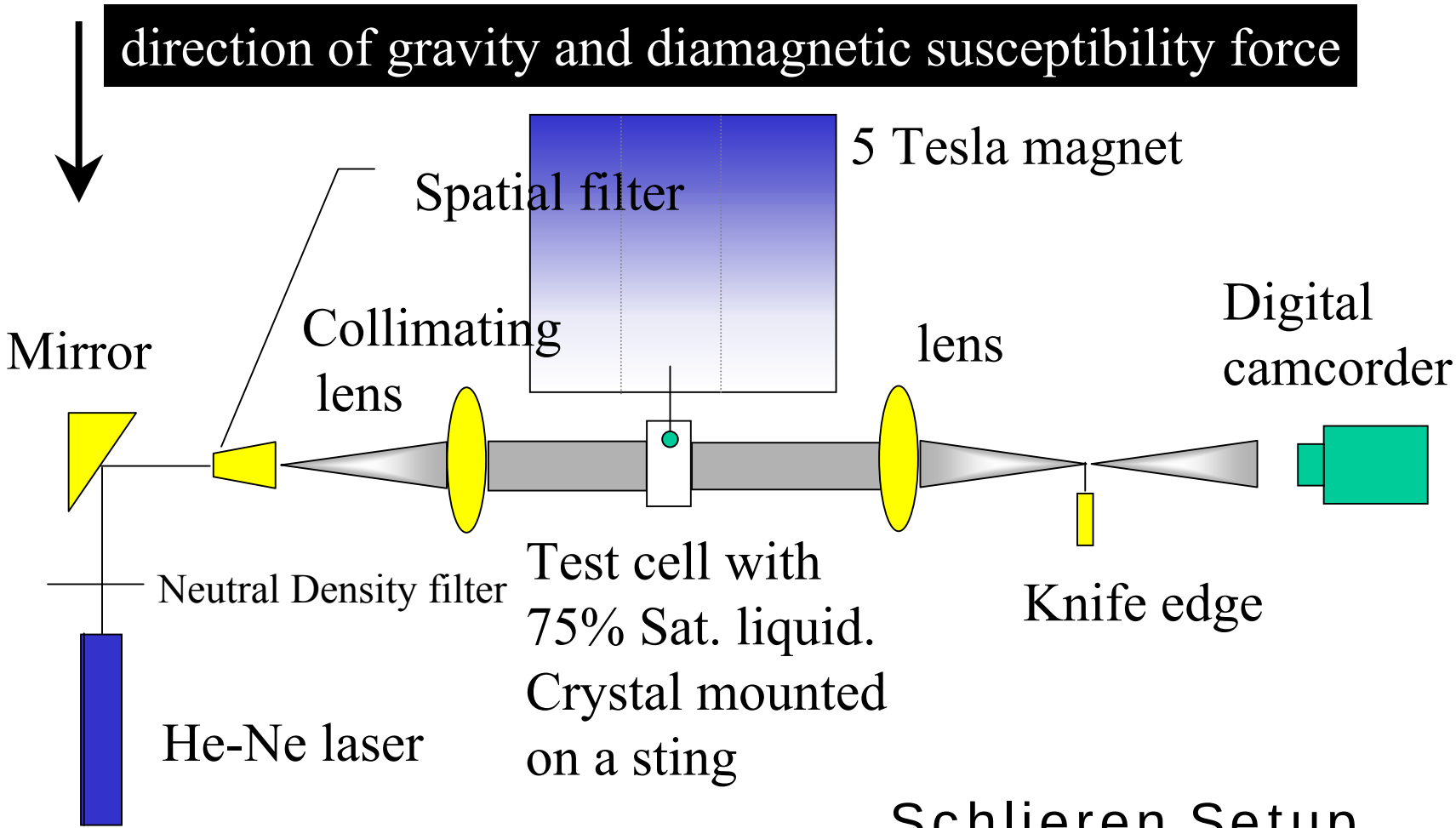
Journal of Crystal Growth. Submitted (2002)

Convection Control Experiment at MSFC

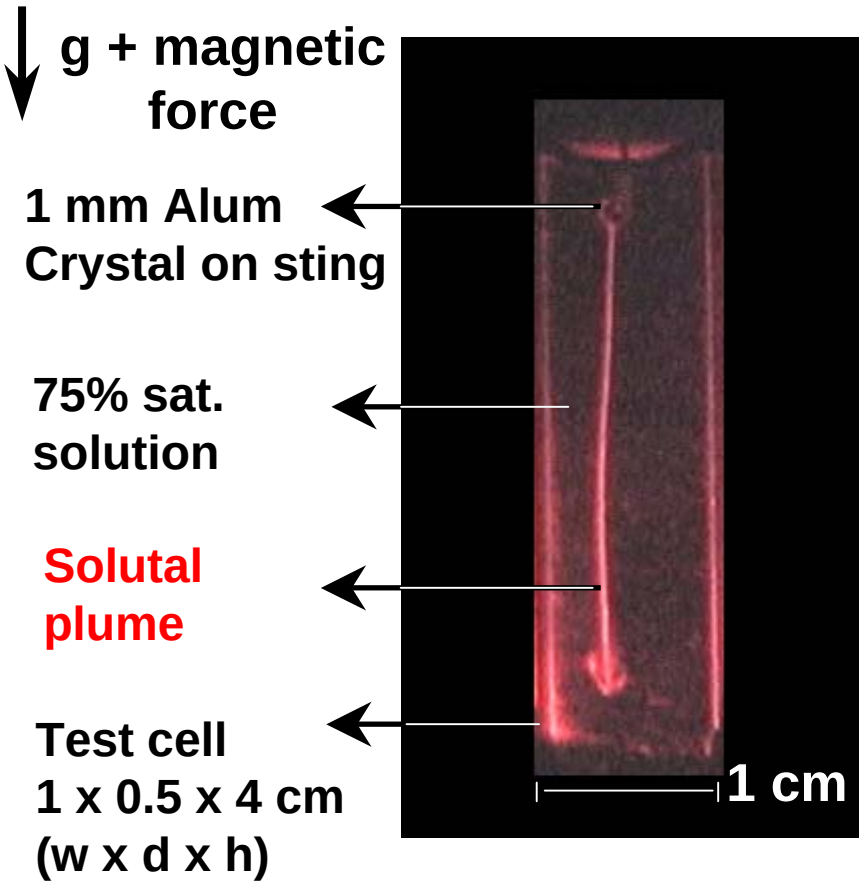
Diamagnetic crystal (Alum) dissolution experiment in 5 Tesla field



Schlieren Setup

Convection Control Experiment at MSFC

Diamagnetic crystal (Alum) dissolution experiment in 5 Tesla field



Schlieren Image

- Average velocity without magnet: ~10.9 pixel/s
- Average velocity with magnet: ~12.73 pixel/s
- Susceptibility effect : 16.7% (assisting gravity)
- 1 week experiment time awarded for follow-up studies at National High Magnet Field Lab., Florida in August 2002

Convection Control Using a Magnetic field

Effect of Lorentz and Susceptibility effects in Protein crystallization

- Protein crystallization is usually carried out using a precipitant such as NaCl, $MnCl_2$, etc. These lend a feeble ionic electrical conductivity ($20\ \Omega^{-1}m^{-1}$) to the solution

- Doing the crystallization in a magnetic field gradient can utilize both the susceptibility and Lorentz effects to damp solutal/thermal convection

- In the presence of a strong magnetic field (~ 10 Tesla) and any fluid convection this results in appreciable Lorentz damping (~ 25% of that due to susceptibility effects alone) (*Magnetic susceptibility effects and Lorentz force damping in Diamagnetic fluids.* N. Ramachandran and F.W. Leslie, 39th AIAA Aerospace Sciences Meeting, Reno, 2001, Paper no: AIAA 2001-0618).

- Typical magnetic gradient field required: (achievable in a magnet)

  $\mathbf{B\partial B/\partial z}$ ~12.5 $Tesla^2/cm$ for balancing thermal convection

  $\mathbf{B\partial B/\partial z}$ ~14.0 $Tesla^2/cm$ for balancing solutal convection

Project Plan and Schedule

Fluid flow studies (2002 – 2003) – Resistive Magnet at NHMFL*

- Paramagnetic and Diamagnetic dissolution experiments
  - Schlieren and Interferometry optics for diagnostics
  - Demonstrate magnetic field effect on solute plume
  - Compare with developed theory
- Levitation experiments
  - Demonstrate levitation of protein crystals in solution
  - Measure effect of magnetic field on solute growth plume

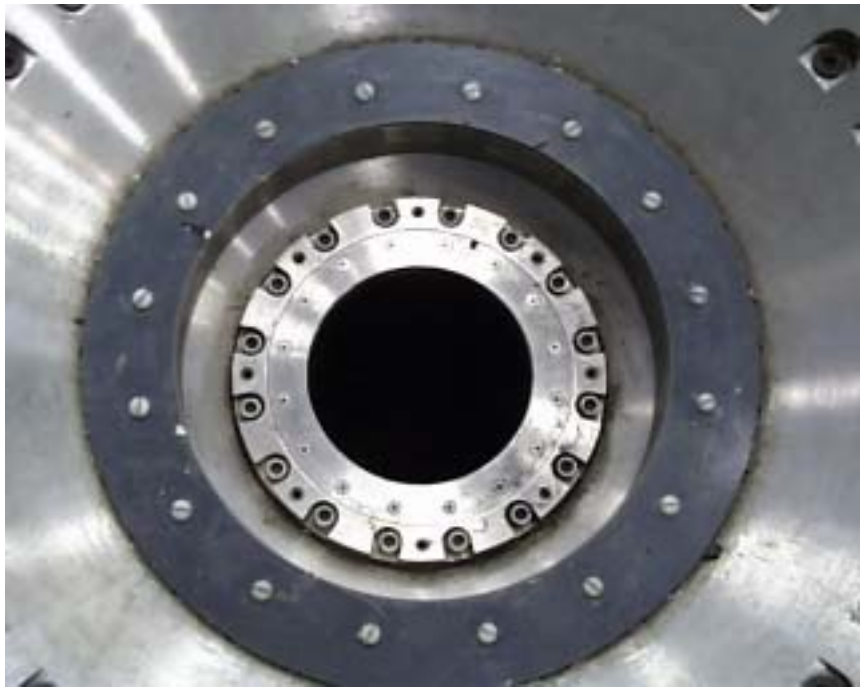
Protein Crystallization studies (2004 – 2006) – SCM^{+} at NHMFL

- Isothermal cell design and diagnostics
- Crystallization of well understood proteins such as thaumatin
- Characterization of grown proteins (x-ray diffraction)
- Crystallization and Characterization of challenging proteins
  - Pyruvate dehydrogenase complex (E1 and E3)

* National High Magnet Field Laboratory, Tallahassee, Florida

$^{+}$ Superconducting magnet

National High Magnet Field Laboratory (NHMFL)
Tallahassee, Florida
CELL 4 - Resistive Magnet used for Fluid flow studies
20 Tesla, 195 mm bore



Top View

Front view

Long Duration Protein Crystallization Studies

SCM 2 – Superconducting Magnet (NHMFL)

19.5 Tesla, 50mm bore resistive magnet

Front view

- Subsequent to fluid flow studies

Tasks (2004 – 2006)

- Crystallization cell design
- Isothermal chamber design
- Positioning
- Benchmark proteins
    - Thaumatin
    - Lysozyme
- Other proteins
    - Pyruvate dehydrogenase

Microporous Materials – Flight definition project in partnership with Dow Chemical Co.

Outstanding Questions

- **Zeolites: What are the structures of the building blocks ?**
- **Where does nucleation occur ?**
- **What are the crystal growth processes ?**
- **What features control morphology - sieve or cage size ?**
- **Is directed synthesis possible ?**
- **Can we model the process ?**

NASA Materials NRA flight definition project to study growth process with *in situ* diagnostics, and modeling (2000 – 2004)

Conventional Growth from a Gel Phase

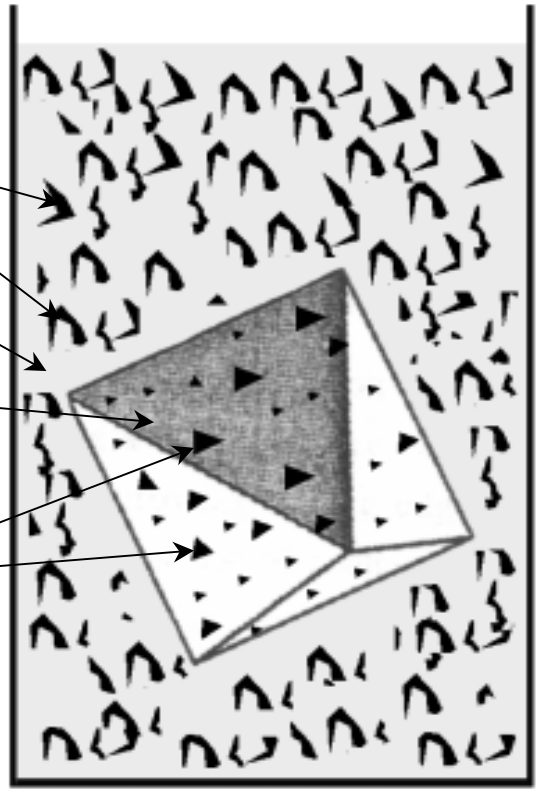
System is opaque precluding diagnostics

Gel Particles

Ions in solution

Growing crystal

Secondary Nucleation sites

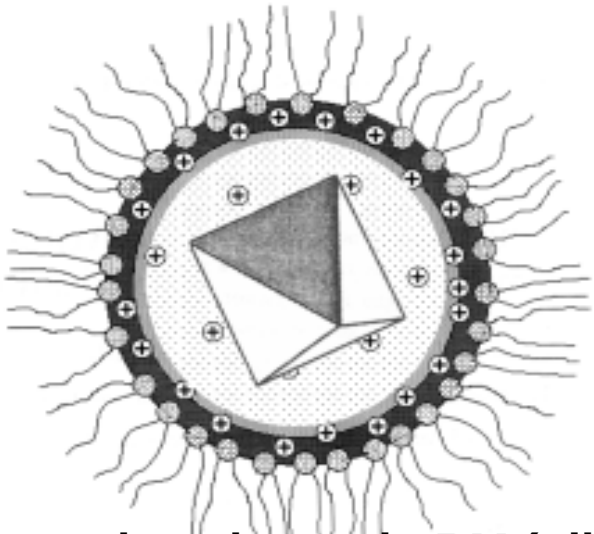


- Crystals nucleate from gel and grow.
- There is direct contact between the gel and the crystal/s.
- Concentration of the precursors varies within the gel and in proximity of the crystal surface (heterogeneous nature of the system).
- Causes multiple-nucleation centers to develop on the crystal surface

Present approach: Growth from Reverse Micelles (RM) - slow kinetics

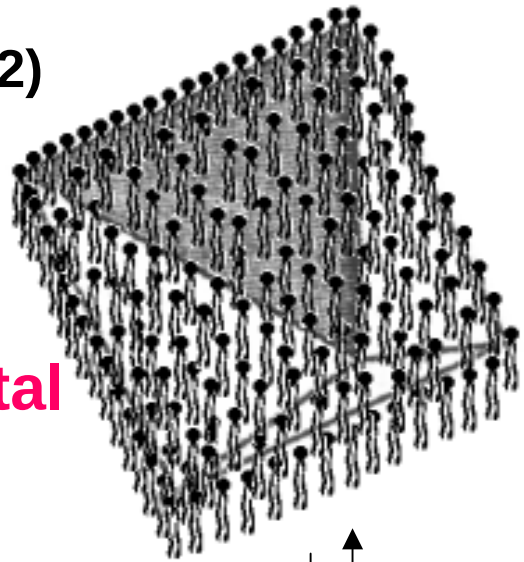
(1)

RM

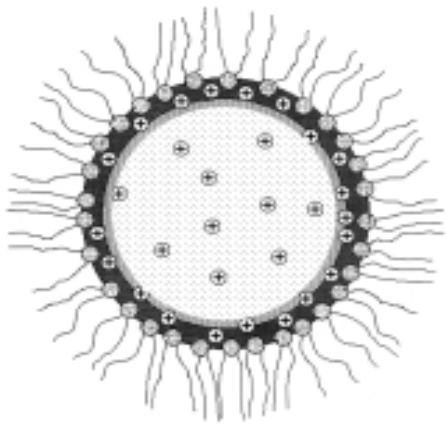


(2)

Crystal



(3)



1. Crystal nucleates in RM (oil-water drop).
2. It comes out of the RM after achieving a certain size. There is a coating of water and surfactant on the crystal.
3. Nutrients are taken up from other RM – they spread into the water layer and provide a uniform concentration of nutrients on the crystal surface for further growth.
4. System transparent

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Modeling aspects

- Microscopic and macroscopic models
- Microscopic approach
  - Population growth model enhancements

    Completed. Now being tested with experiments
  - DLVO theory; inclusion of density differences in problem formulation and calculations
- Macroscopic approach
  - solutal convection calculations with growth rate incorporated. Initiated
  - two phase calculations (sedimentation effects)

Project de-scoped to ground investigation. New NRA proposal in the works.

Appendix C

Biotechnology Science Team

Title	Presenter	Page
Biotechnology Science Introduction	Dr. Robert Richmond	B-1
"Flight Hardware Development and Research at MSFC for Optimizing Success on the International Space Station"	Dr. Russell Judge	B-2
"Structural Biology of Proteins of the Multi-enzyme Assembly Human Pyruvate Dehydrogenase Complex"	Dr. Ewa Ciszak	B-10
"Cell Science and Cell Biology Research at MSFC: Summary"	Dr. Ronald Young Dr. Robert Richmond	B-13
"Growth Defects in Biomacromolecular Crystals"	Dr. Alexander Chernov	B-30
"New Directions in Biotechnology"	Dr. Marc Pusey	B-53
"The Building Blocks of Materials: Gathering Knowledge at the Molecular Level"	Dr. Sridhar Gorti	B-59
"New Programs Utilizing Light Scattering and Flow Imaging Techniques for Macromolecular Crystal Growth and Fluid Dynamics Studies"	Dr. Phil Segre	B-69
"Biotechnology Protein Expression and Purification Facility"	Dr. Laurel Karr	B-79

BIOTECHNOLOGY SCIENCE PRESENTATION 6/18/02

Areas of In-House Research

• In-house Flight Project Research	Alex Chernov
• In-house Flight Technical Research	Russell Judge
• Structural Biology	Ewa Ciszak
• Cell Biology	Ron Young
• Ground-Based and Startups 1	Phil Segre
• Collaborations and Startups 2	Sid Gorti
• New Areas	Marc Pusey

Areas of Research are presented to focus the breadth of in-house research

Funded or Science Program supported research projects are presented

- **Flight Project Research - NRAs; microgravity-unique reasons for space crystals**
- **Flight Technical Research - 1 hardware development NRA; modeling for user-assistance**
- **Structural Biology - 2 NRAs, 1 NIH; advancing in-house structures for flight and science**
- **Cell Biology - 1 DoD; muscle physiology, cancer risk assessment**
- **Ground-based and Startups 1 - 1 NRA; new science program area (light scattering)**
- **Collaborations and Startups 2 - new science program area (atomic force microscopy)**
- **New Areas - OBPR-related directions; using old ways for new ways**

Abstract

Flight hardware development and research at MSFC for optimizing success on the International Space Station

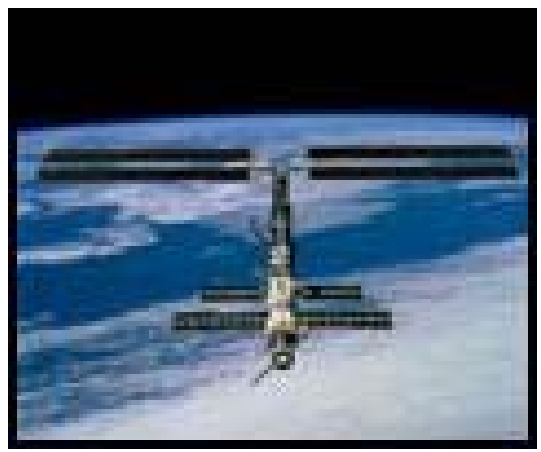
Dr. Russell Judge

To optimize biological crystallization success in microgravity in-house personnel at the MSFC are working on the development of innovative flight hardware such as Delta-L and the Iterative Biological Crystallization (IBC) apparatus as well as trouble shooting the performance of existing hardware.

Delta-L will provide a diagnostic hardware to examine the relationship between crystal growth characteristics and crystal quality improvement in microgravity. IBC is a new hardware being designed to allow iteration of crystal growth experiments in microgravity using innovative 'lab on a chip' technology. While being built to obtain scientific data of benefit to the scientific community, the design methods involved in the development of these hardware have directly benefited other groups within NASA and keep NASA at the forefront of innovation.

Flight hardware development and research at MSFC for optimizing success on the International Space Station

Dr. Russell Judge



MSFC technical research

- To enhance crystallization success in microgravity, the biological science team at the MSFC is involved in;
  - providing innovative design techniques and flight hardware
  - trouble shooting existing hardware

- Beyond crystal growth these activities:
  - Directly benefit other design groups within NASA
  - Keep MSFC at the forefront of innovation.

Delta-L

- Structural crystallography requires large, high quality crystals.
- Previous work in microgravity reports improved crystal quality for approx. 20% of the macromolecules flown.
- Delta-L is a diagnostic hardware being developed to investigate a proposed correlation between crystal growth characteristics and crystal quality improvement in microgravity, with the aim of developing criteria to select which macromolecules will benefit most from microgravity.

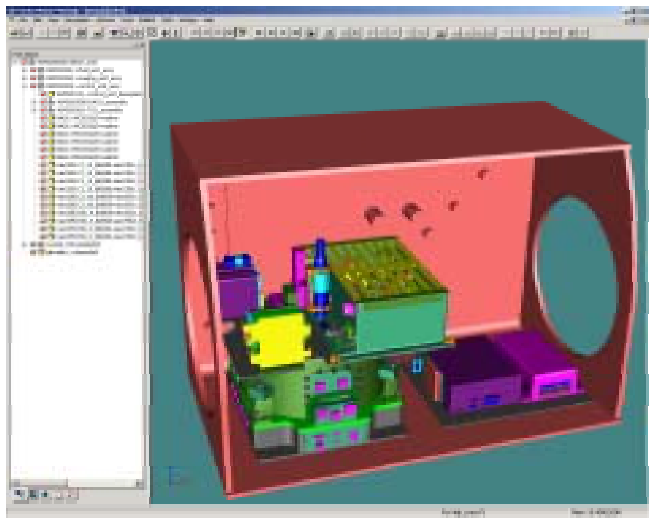
Delta-L

- Fast track, low cost hardware development using a small in-house project team.
- Initial design to flight hardware in approx. 2 years.

Outcome

Interaction of onsite team and NASA management enhanced speed of hardware development

- Web based virtual design software, iMAN, facilitated better team communication

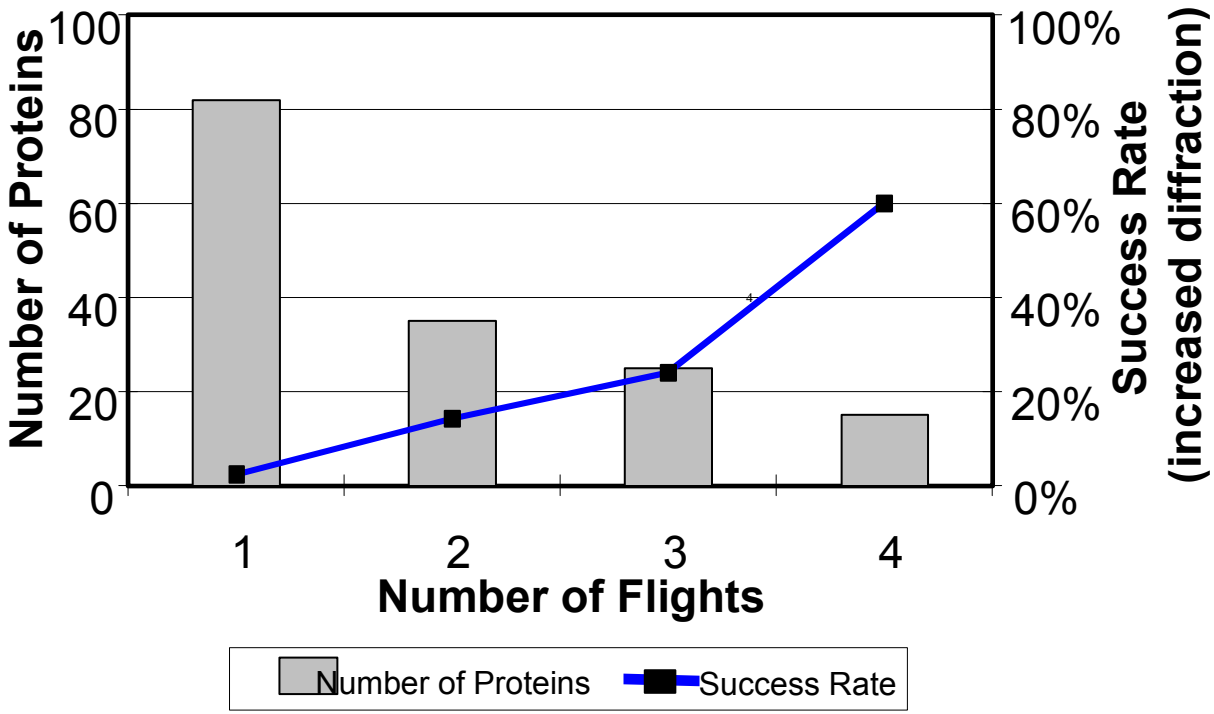


Outcome

First time used on a flight project. Now being used for other MSFC hardware.

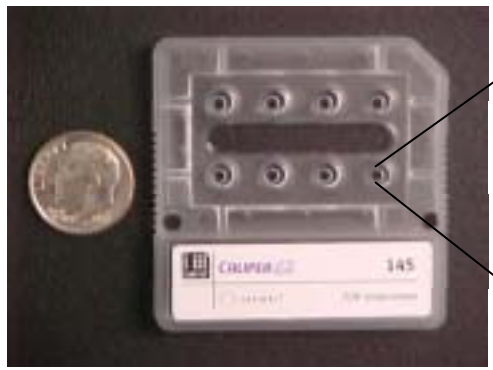
Iterative Biological Crystallization

- Iterations are important for crystallization success in microgravity (Kundrot et al., 2001, *Crystal Growth & Design*, 1: 87-99.
- IBC provides new hardware that supports the iterative nature of improved crystal growth methods.

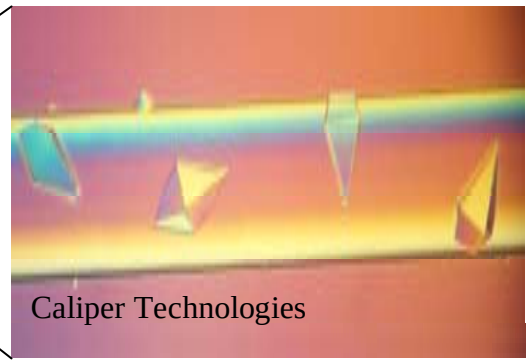


IBC

- IBC in collaboration with Caliper Technologies® will use innovative 'lab on a chip' technology to provide a novel advanced platform for crystallization on the ISS.



Standard LabChip™ device



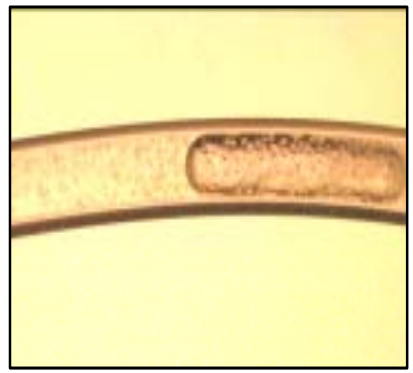
Thaumatin crystals grown in LabChip™ channel

Outcome

Novel flight hardware produced in-house at MSFC using cutting edge technology.

Troubleshooting

- For the Enhanced Gaseous Nitrogen Dewar (EGN) crystallization solutions are loaded in tubing and snap frozen in liquid nitrogen. On orbit the solutions thaw and crystallize.



- Many returning tubes contained bubbles greatly reducing the reproducibility of the experiments.

- Ciszak et al, 2002, ("Use of Capillaries for Macromolecular Crystallization in a Cryogenic Dewar." Ciszak, E.; Hammond, A.S.; Hong, Y.S. Crystal Growth & Design. 2002. 2(3); 235-38.) developed an alternative freezing technique that was tested on flight 7A.

- The method was successful and eliminated the bubble problem.

Outcome

In-house MSFC personnel are improving existing flight hardware performance.

♦Title: Structural Biology of Proteins of the Multi-enzyme Assembly Human Pyruvate Dehydrogenase Complex

♦PI Ewa Ciszak

OBJECTIVES and RESEARCH CHALLENGES:

1. Need to establish Human Pyruvate Dehydrogenase Complex protein crystals
2. Need to test value of microgravity for improving crystal quality of Human Pyruvate Dehydrogenase Complex protein crystals
3. Need to improve flight hardware in order to control and understand the effects of microgravity on crystallization of Human Pyruvate Dehydrogenase Complex proteins
4. Need to integrate sets of national collaborations with the restricted and specific requirements of flight experiments
5. Need to establish a highly controlled experiment in microgravity with a rigor not yet obtained
6. Need to communicate both the rigor of microgravity experiments and the scientific value of results obtained from microgravity experiments to the national community
7. Need to advance the understanding of Human Pyruvate Dehydrogenase Complex structures so that scientific and commercial advance is identified for these proteins

MSFC STRUCTURAL BIOLOGY RESEARCH

♦CHALLENGE:
Crystallization of multienzyme complexes is usually difficult.

♦OBJECTIVES:
(1) Demonstrate effects of microgravity on the growth of crystals of Human Pyruvate Dehydrogenase Complex (hPDC) proteins.
(2) Employ the Enhanced Gaseous Nitrogen Dewar in microgravity to test for the quality of hPDC protein crystals relative to their earth grown counterparts.
(3) Use space-quality crystals to facilitate the three-dimensional structure determination of this multi-enzyme complex.
(4) Support the objectives of the Structural Biology Test program.

♦PURPOSE:
Determine significance of microgravity on the growth of crystals of generally difficult to crystallize proteins from a multienzyme complex.

Photograph of yellow crystals of, hPDC protein, humanE3 containing the cofactor FAD

APPROACH

♦HYPOTHESIS:
The effects of microgravity on the crystallization of hPDC proteins can be established and their benefits be quantified.

♦RESOURCES:
two NRA grants
one NIH grant

♦FACILITIES:
(1) MSFC Laboratory of Structural Biology
(2) Brookhaven National Laboratory Synchrotron
(3) Argonne National Laboratory Synchrotron
(4) Enhanced Gaseous Nitrogen (EGN) Dewar

VALUE and BENEFIT

♦WHY DO THIS RESEARCH:
Establishing if microgravity facilitates the enhanced growth of PDC protein crystals will shed considerable light on the value of microgravity-assisted crystallization as it pertains to multi-enzyme complexes as specifically addressed by the National Research Council in a recent review of the NASA microgravity research program.

♦WHO WILL BENEFIT:
1) the biomedical industry.
2) the pharmaceutical industry.
3) the field of macromolecular crystallography
4) the NASA Microgravity Biotechnology Program

FLYING FOR STRUCTURE IN THE ENHANCED GASEOUS NITROGEN DEWAR

Obtain biomolecular crystals in low gravity environment

- The EGN is used to provide crystals from the low gravity environment for studies of their morphology and internal structure
- Components of Pyruvate Dehydrogenase Complex will be flown in the EGN in order to test whether microgravity can assist the crystallization of these large proteins

Crystals photographed under a microscope, grown during STS-106 in the EGN Dewar. The solution that grew these crystals and others were prepared by students. (Courtesy of the University of California at Irvine.)

How: The Cryogenic Dewar contains hundreds of crystallization solutions that are confined in plastic capillary tubes. While on-orbit, solutions thaw, mix, and begin forming crystals, which continue to grow for several more weeks. Crystals are retrieved following return from a mission.

Impact: Provide crystals from the low gravity environment for studies of their morphology and internal structure

Unique resource for obtaining large crystals that can be used in neutron diffraction studies

Large sample size allows for test of reduced convection in the microgravity environment

Cell Science & Cell Biology Research at MSFC: Summary

Dr. Ronald B. Young: Skeletal Muscle Atrophy and Muscle Cell Signaling
Dr. Robert Richmond: Radiation & Cancer Biology of Mammary Cells in Culture

The common theme of these research programs is that they investigate regulation of gene expression in cells, and ultimately gene expression is controlled by the macromolecular interactions between regulatory proteins and DNA. The NASA Critical Path Roadmap identifies "Muscle Alterations and Atrophy" and "Radiation Effects" as Very Serious Risks and Severe Risks, respectively, in long term space flights.

The specific problem addressed by Dr. Young's research is that skeletal muscle loss in space cannot be prevented by vigorous exercise. Aerobic skeletal muscles (i.e., red muscles) undergo the most extensive atrophy during long-term space flight. Of the many different potential avenues for preventing muscle atrophy, Dr. Young has chosen to study the β-adrenergic receptor pathway. The reason for this choice is that a family of compounds called β-Adrenergic Receptor (βAR) agonists will preferentially cause an increase in muscle mass of aerobic muscles (i.e., red muscle) in animals, potentially providing a specific pharmacological solution to muscle loss in microgravity. In addition, muscle atrophy is a widespread medical problem in neuromuscular diseases, spinal cord injury, lack of exercise, aging, and any disease requiring prolonged bedridden status. Skeletal muscle cells in cell culture are utilized as a model system to study this problem.

Dr. Richmond's research is directed toward developing a laboratory model for use in risk assessment of cancer caused by space radiation. This research is unique because a human model will be developed utilizing human mammary cells that are highly susceptible to tumor development. This approach is preferential over using animal cells because of problems in comparing radiation-induced cancers between humans and animals.

Cell Science & Cell Biology Research at MSFC

Dr. Ronald B. Young: Skeletal Muscle Atrophy and Muscle Cell Signaling

Dr. Robert Richmond: Radiation & Cancer Biology of Mammary Cells in Culture

Unifying Theme of Research in Relation to Overall Program at MSFC:

- **Investigations into control of gene expression**
- **Gene expression is ultimately controlled by regulatory proteins and the macromolecular interactions of these proteins with DNA promoter regions**
- **Structural information about these macromolecular interactions is necessary to fully understand control of gene expression in cells**

From NASA Critical Path Roadmap (CPR)

- 8 Critical Risk Areas are defined
    - Bone Loss
    - Cardiovascular Alterations
    - Human Behavior and Performance
    - Immunology, Infection, and Hematology
    - **Muscle Alterations and Atrophy**
    - Neurovestibular Adaptation
    - **Radiation Effects**
    - Clinical Capability
- In ranking these Risks on a 10-category scale from Serious (1) to Severe (10),
    - **Muscle Alterations and Atrophy** ranks as a Very Serious Risk (9)
    - **Radiation Effects** ranks as a Severe Risk (10)

Dr. Ronald B. Young, Research Interests:

Specific Problem: Skeletal Muscle Loss in Microgravity Cannot Be Prevented By Vigorous Exercise.

Broader Implications: Understanding and Preventing Muscle Loss is a More General Medical Problem, including:

- Neuromuscular Diseases,
- The Aging Process,
- Spinal Cord Injury,
- Inactivity Due to Sedentary Life Style,
- Any Long Term Illnesses Requiring Bed Rest,
- Agricultural Implications in Increased Efficiency of Meat Production

General Concept:

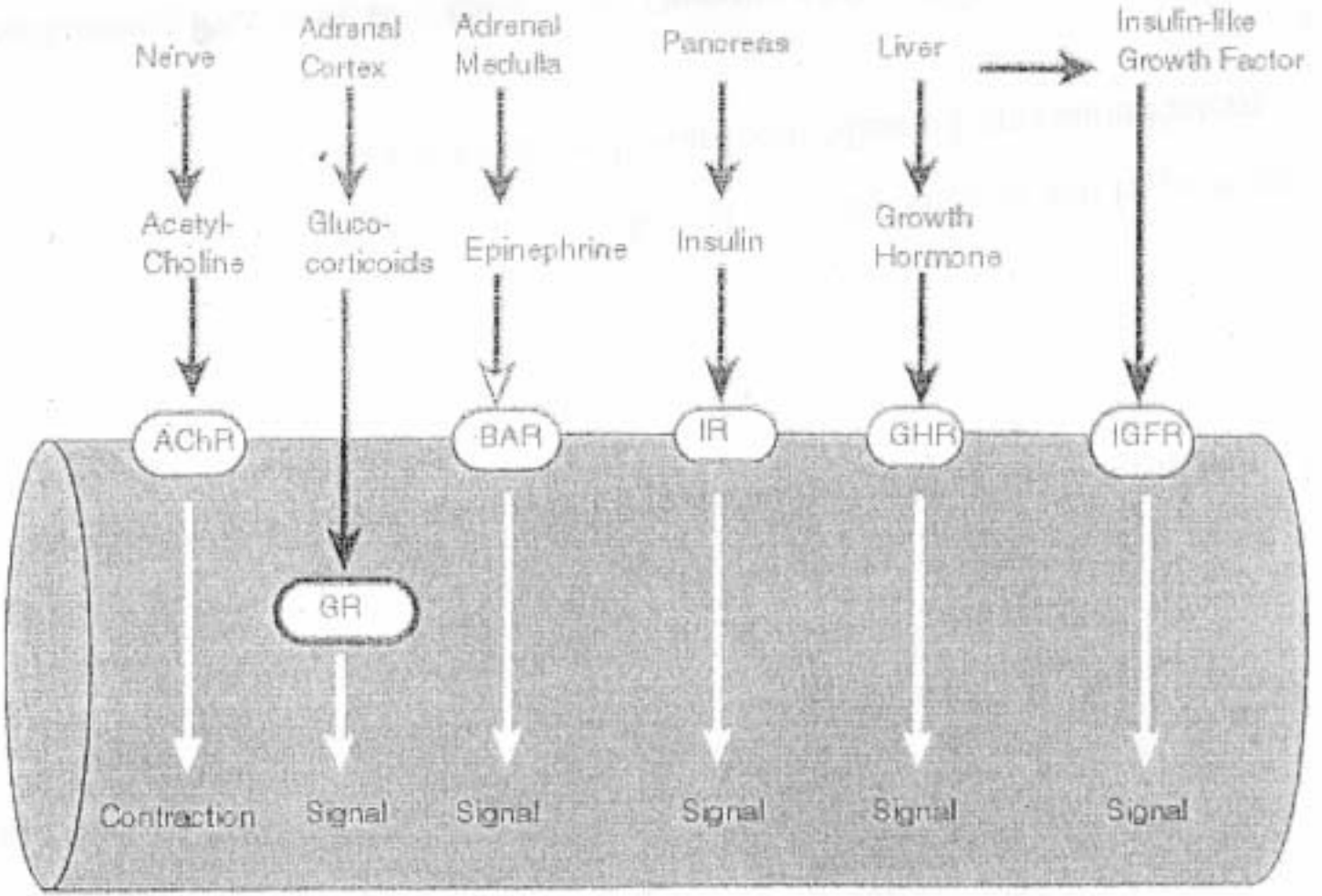
- **Muscle Cells Respond to Numerous External Signals to Increase or Decrease Muscle Mass. How this Process Works is Poorly Understood.**

- **Atrophy/Hypertrophy Presumably Due to Changes in One or More Signaling Processes.**

Specific Approach:

- **Use Muscle Cells in Cell Culture as a Model to Study Atrophy and Hypertrophy**
  - **Muscle Cells Differentiate Toward Red Muscle Expression Pattern**

- **Stimulating Receptors Will Change the Quantity of Protein in Muscle Cells**
  - **Artificial Activation of β-Adrenergic Receptor Signal Increases Muscle Protein**
  - **Artificially Blocking Acetylcholine Receptor Decreases Muscle Protein**


Nerve
Adrenal Cortex
Adrenal Medulla
Pancreas
Liver
Insulin-like Growth Factor
Acetyl-Choline
Gluco-corticoids
Epinephrine
Insulin
Growth Hormone
AChR
BAR
IR
GHR
IGFR
GR
Contraction
Signal
Signal
Signal
Signal
Signal

Why Study β-Adrenergic Agonists?

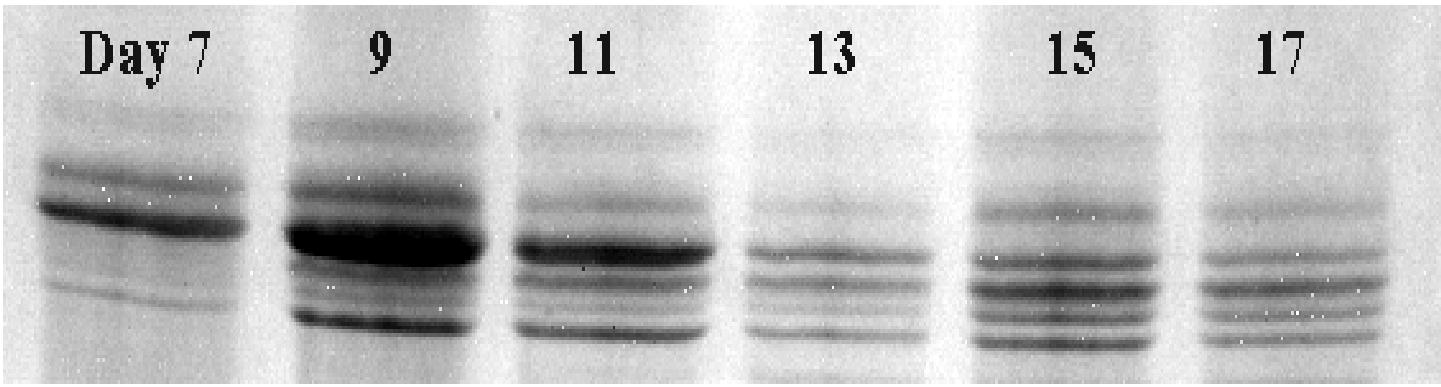
- Aerobic skeletal muscles (i.e., red muscles) undergo the most extensive atrophy during long-term space flight, and this cannot be prevented entirely by vigorous exercise.

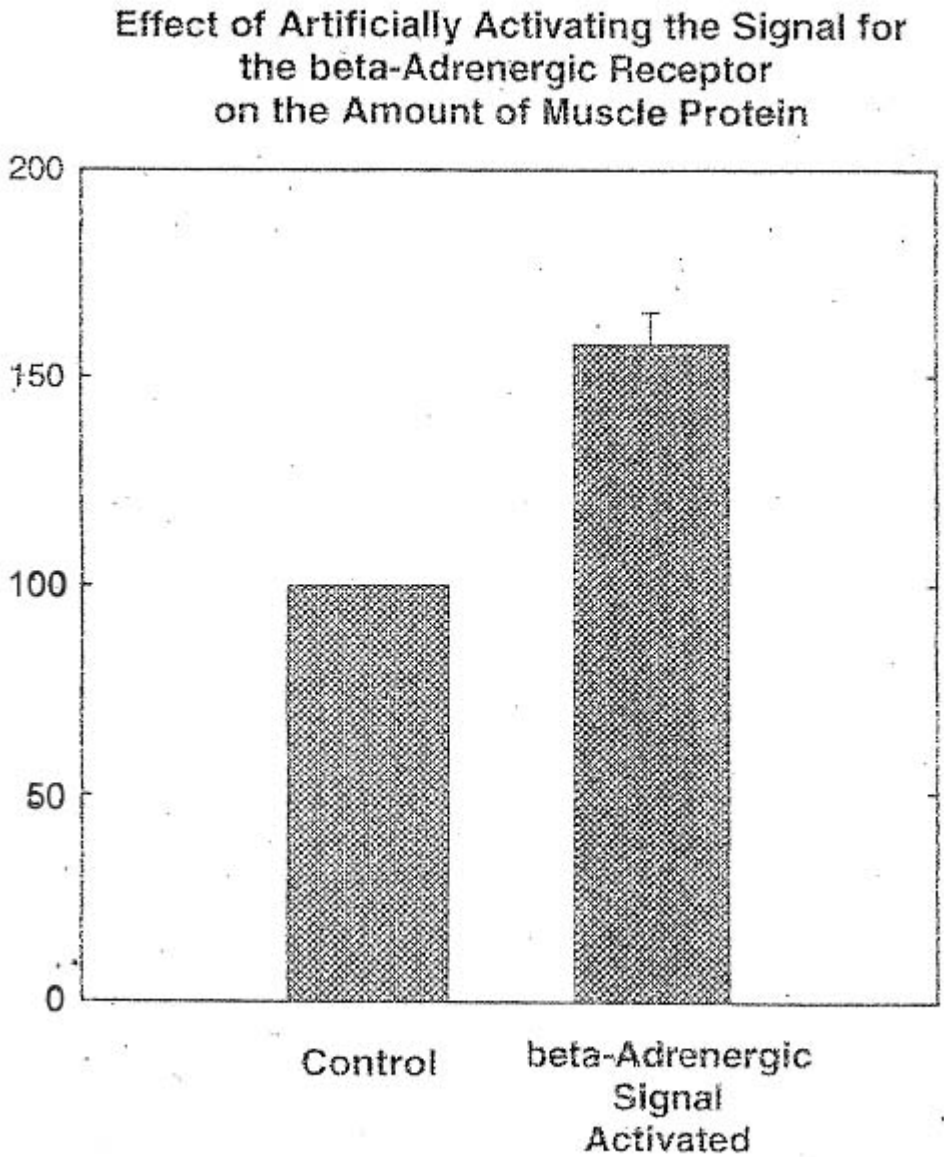
- A family of compounds called β-Adrenergic Receptor (βAR) agonists will cause an increase in muscle mass of aerobic muscles (i.e., red muscle) in animals. However, βAR agonists have not been approved for use in humans.

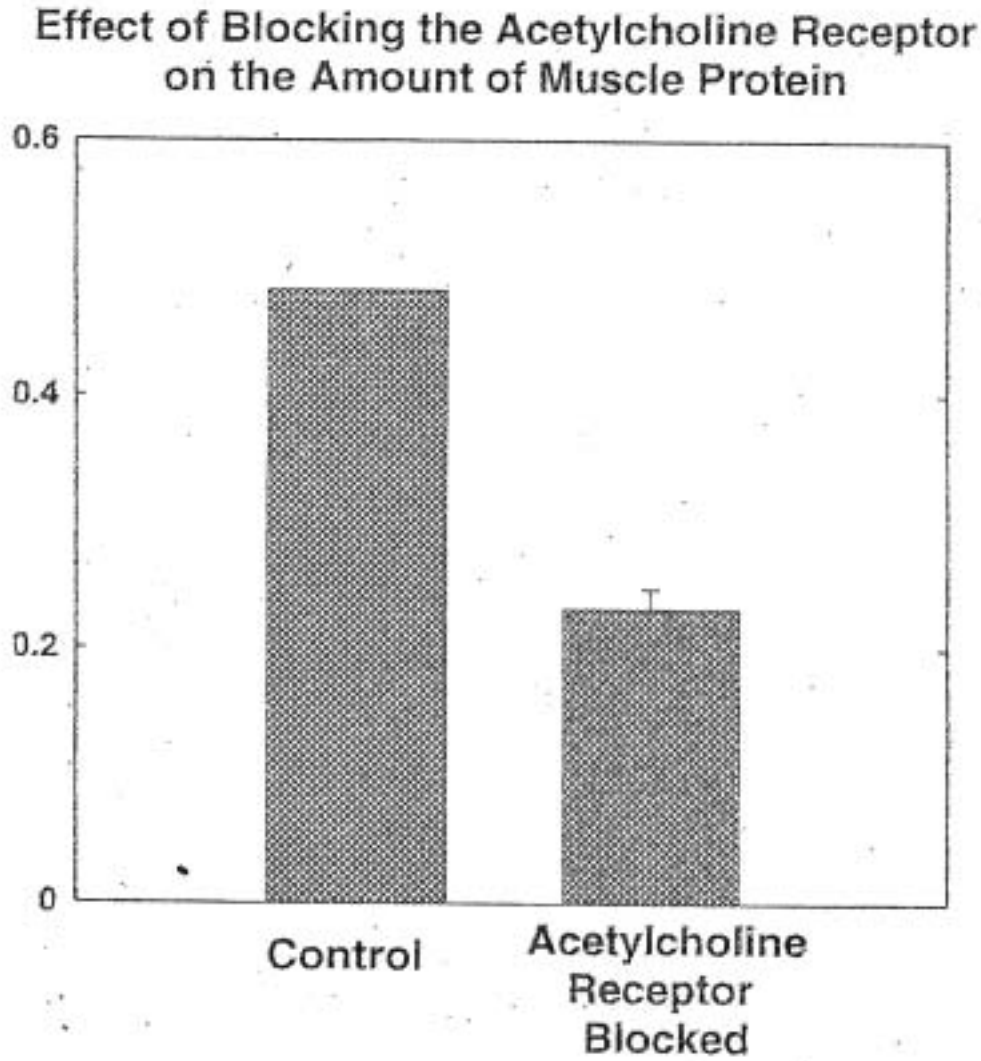
- The changes in gene expression caused by βAR agonists that in turn lead to muscle hypertrophy in animals are not known.

Developmental changes in expression of five muscle myosin heavy chain protein isoforms during differentiation of C2C12 muscle cells in Cell Culture.

- Separation of proteins was carried out by polyacrylamide gel electrophoresis.
- The expression pattern in this model system after 15-17 days in culture strongly resembles the pattern found in aerobic skeletal muscle of adult animals.




Effect of Artificially Activating the Signal for
the beta-Adrenergic Receptor
on the Amount of Muscle Protein
200
150
100
50
0
Control
beta-Adrenergic
Signal
Activated


Effect of Blocking the Acetylcholine Receptor
on the Amount of Muscle Protein
0.6
0.4
0.2
0
Control
Acetylcholine
Receptor
Blocked

Impact:

•Understanding muscle hypertrophy by βAR agonists may lead to new approaches for preventing muscle atrophy during space flight.

•Muscle atrophy is a widespread medical problem in neuromuscular diseases, spinal cord injury, lack of exercise, aging, and any disease requiring prolonged bedridden status.

•Possible development of a drug screening process for discovering new βAR agonists or other drugs that could be approved for use in astronauts without adverse side effects.

Future Work on β-Adrenergic Receptor & Muscle Atrophy:

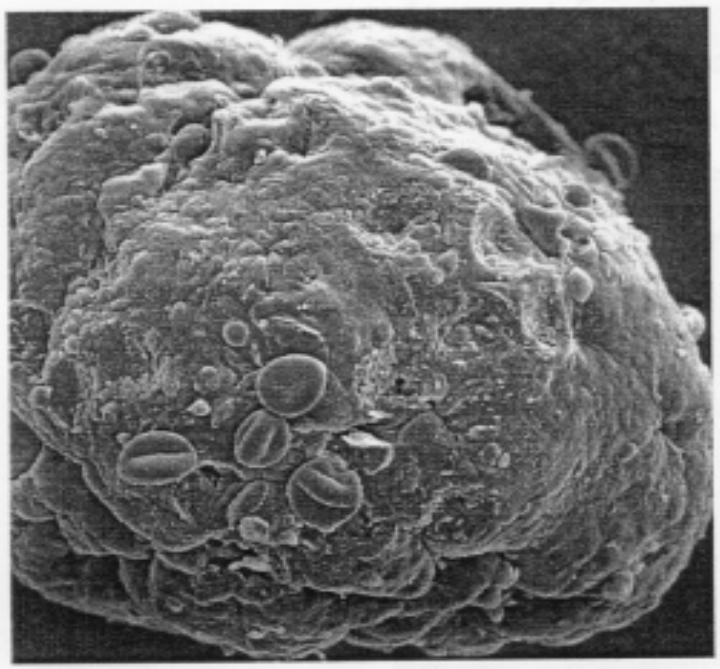
- **β-Adrenergic Agonist Effects on Hypertrophy**
  - Screening assay for muscle proteins in cell cultures
  - Look for subtle effects rather than drastic effects
- **How Signaling pathway works**
  - Is cyclic AMP really the signal involved in muscle hypertrophy?
  - What causes synergistic effect between epinephrine and β-adrenergic agonists?
- **DNA Microarray Analysis of Gene Expression**
  - Study expression of thousands of genes at a time
  - Which genes are up-regulated or down-regulated by β-adrenergic agonists

Dr. Richmond's research is directed toward developing a laboratory model for use in risk assessment of cancer caused by space radiation.

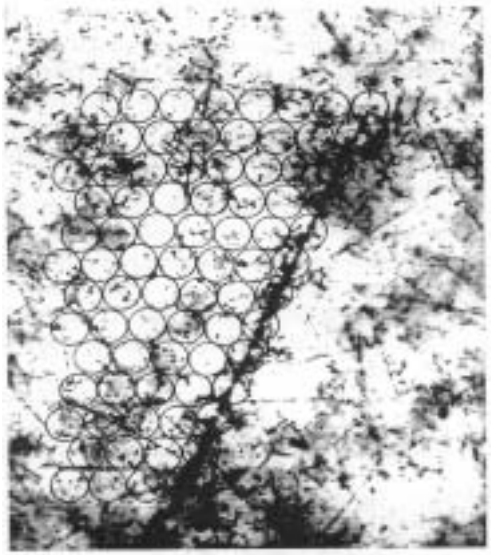
The radiation health research priorities for enabling long-duration manned space-flight missions were established in the 1996 NRC Report entitled "Radiation Hazards to Crews of Interplanetary Missions: Biological Issues and Research Strategies". This report emphasized that a 15-fold uncertainty in predicting radiation-induced cancer incidence must be reduced before NASA can conduct extended HEDS missions. The report concludes that the great majority of this uncertainty is biologically based.

An experimental human cell model is useful for estimating cancer risks caused by space radiation. The value for developing such a model is based on the following assumptions.

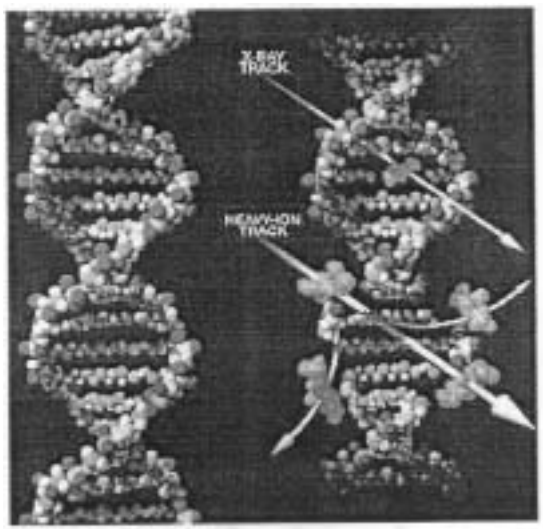
1. An experimental model will provide the precision of results needed to eliminate experimental uncertainty associated with current radiation-induced cancer risk assessment.
2. A human model, as opposed to an animal model, is required for risk assessment because of problems in comparing radiation-induced cancers between humans and animals.
3. A human cell model can be made relevant:
   a. it can be based on cells that are involved in the major categories of human cancers;
   b. for solid tumors, it can include tissue-equivalence, e.g., 3-dimensional cell culture in the NASA Bioreactor that promotes differentiation similar to that of normal tissue.



Different kinds of radiation are encountered in space

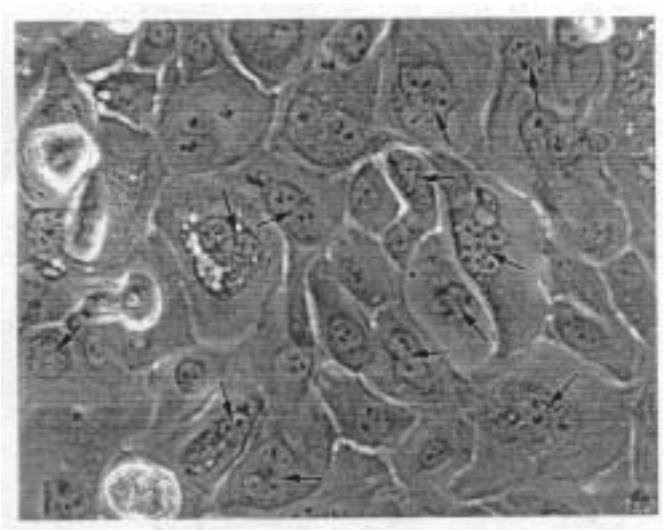


and lead to different biological outcomes following interaction with cells



Radiation-induced changes in cells can be analyzed as indicators of cancer probability such as changes in chromosome abnormalities

And in presentation of unusual nuclei in irradiated cells.



PUBLICATIONS IN REFEREED JOURNALS

Young, R.B. K.Y. Bridge, A.J. Wuethrich, and D.L.Hancock. Effect of Serum from Chickens Treated with Clenbuterol on Myosin Accumulation, β-Adrenergic Receptor Population, and cyclic AMP Synthesis in Embryonic Chicken Skeletal Muscle Cell Cultures. In Vitro Cell. and Dev. Biol. 38: 102-110.

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Growth Defects in Biomacromolecular Crystals

Dr. Alexander Chernov

Outline

- Biomacromolecular crystallization
  - General framework
  - 20 years of NASA program
  - Statement of the problem
- Impurities in protein crystal growth
  - Protein purity and crystal quality
  - Distribution coefficient
  - Cleaner crystals from space
  - Impurity depletion zone and diffusional purification
  - Canavalin

Summary

Dr. Alexander Chernov

NASA ground based program confirmed close similarity between protein and small molecules crystal growth, but also revealed essential differences.

No understanding exists as to why and when crystals grown in space are, in ~20% of cases, of higher quality. More rationale is needed in flight experiments.

Ferritin crystals grown in space are ~2.5 times cleaner than their terrestrial counterparts. This may occur because of existence of a zone depleted with respect to impurities around a crystal growing in stagnant solution. This zone should appear since distribution coefficient. for homologous impurities exceeds unity. This impurity depletion zone hypothesis requires verification and development. Thorough purification from homologous impuritites brought about resolution improvement from 2.6 to 1.8A for ferritin and from 2.6 to 2.OA for canavalin.

See the attached text, "Biomacromolecular Crystallization" for more details and view on the NASA biocrystallization program.

Biomacromolecular Crystallization

General Framework

- **Biological macromolecules:**

  Proteins, nucleic acids, their complexes (e.g., viruses)

- **Biology needs: spatial arrangements of atoms in a macromolecule to understand its function**

- **Industry needs: new drugs, protein production (grain shape, size, purity)**

- **Approach:**
  - **grow crystals of these macromolecules**
  - **shine X-rays**
  - **find structure from diffraction pattern**

- **Crystallization:**
  - **produce and purify protein**
  - **dissolve it**
  - **add precipitant, change pH, temperature to reduce protein solubility and induce crystallization.**

- **Bottleneck problem: find the crystallization conditions to grow high quality crystals**

- **Strategies:**
  - **automation for structural genomics, proteonics: ~10,000 droplets/day, <50% success, "mineralogical collection“**
  - **scientific approach: understanding of solubility, interactions in solution, nucleation, crystallization, crystal perfection, ultrapurification, screening, mutagenesis.**

Biomacromolecular crystallization and microgravity

Dr. Alexander Chernov

An essential part of the problem with the Biocrystallization in space is lack of scientific background of why and when crystallization in space results in more perfect crystals, allowing better structural resolution (in ~ 20% of cases) We still do not know for sure if space is a must.

This lack of knowledge prevents rationale for designing systematic protein crystallization experiments that enhance our probability of success. Fundamental ground-based programs from NASA, as well as ESA, Canada, and NASDA, did a good job in laying down/confirming (sometimes on a quantitative level) the basic laws of protein crystallization, much in common with the inorganic crystal growth, though showing crucial differences. However, in the flight program, the "let us see what happens" approach, acceptable only at the very onset of the Program (beginning of the 80's,) is still in place and is retarding the potential value for outcome.

The Program needs to support the rational and rigorous approach recently emerging in order to understand the role of microgravity in sporadic empirical findings and to continue the effort, including flight crystalization experiments, on a solid scientific background. Developments of the last 5 years have provided space-unique hypotheses for biocrystallization in space [1-9].

The first space-unique hypothesis [1-8] is based on results from space experiments and also from ground-based findings. The space experiments [5] showed that the crystals grown in space (ferritin), under convection-free conditions contain fewer impurities. Since long ago, high crystal purity is well known to improve crystal quality [8] because impurity produces internal stress and disorder in crystals [2]. The reason for the higher purity of crystals in space may be as follows[2,3,4,5]: The homologous impurities (like dimers or other species closely related to the crystallizing protein) are preferentially trapped by growing crystals [4,5,6]. Therefore, at the initial stages of growth, a small growing crystal traps the impurities from the surrounding stagnant solution and creates the impurity depletion diffusion zone around itself [3.4,5,6,7]. This zone expands and deepens (i.e. becomes even more clean) as the crystal grows, so that further growth occurs from ever-cleaner solution. This is diffusion filtration: the impurity species have to cover an ever-increasing path to diffuse to the growing interface through the impurity depletion zone. This hypothesis explains inferior ground-based controls because even weak

Cont. next slide

convection (at the flow rate ~ 10-20 m/s) present under terrestrial conditions [7] destroys the impurity depletion zone, increases the impurity access to the growing crystal, and thereby deteriorates the crystal quality. It is critical that added experimental information now be gathered for scientific proof or disproof of this hypothesis. If successful, it allows developing more rational experimental designs for crystallization experiments, both on earth and in space.

The second, related, hypothesis is that striation in homogeniety develop within a crystal due to bunching of growth steps. These striations were found in the ground-grown lysozyme crystals[9]. Both the bunching and striations may be caused by impurities. Bunching allows, also, for trapping of the regular, but misaligned protein molecules. These phenomena have not yet been tested for space-grown crystals, but are known to occur in conventional inorganic crystal growth.

The third hypothesis is not space-unique and is often repeated in the literature [8]. This is that depletion of the crystallizing protein at the surface of the growing crystal decreases supersaturation at it and, therefore, improves crystal quality. Lower supersaturation at the growing interface and the corresponding higher crystal quality is a well-established fact for inorganic crystal growth, but low supersaturation may be achieved under terrestrial conditions even easier than in space. While any level of supersaturation may be achieved on earth, the diffusion purification cannot unless gel media is used. The gels, however, chemically interact with crystals and macromolecules.

Deep purification might be, and sometimes is, a solution. However, homologous impurities are well known to spontaneously appear from regular species, often within the timescale comparable to that of crystallization (weeks ~ months). Such protein ageing is also known, but is not addressed. Also, the existing protocols of protein extraction and purification results in low degree of purity (< 95% or worse, sometimes 50%,) and are aimed mainly at purification from foreign rather than from homologous species. For comparison, purity of inorganic salts for crystallization is ~ 99.999% for and reaches 99.99999999% for semiconductor silicon.

The biomacromoleculer crystallization is a big area. There are hundreds of thousands of types of biomacromolecules crucial for life. Only the human genome includes ca. 50, 000 of proteins. The function of macromolecules is determined by their spatial atomic arrangements. These arrangements may be found now only by X-ray diffraction from perfect crystals (The significance of nuclear magnetic resonance and

two-dimensional crystallization is very limited. These are mainly auxiliary tools in this respect). Therefore, structural biology is the major subject of many tens if not hundreds of laboratories. X-ray structural determination now is a matter of several weeks or month and will be fully automated in ~ 5 years. Crystallization takes from several months to years. Thus, crystallization is becoming more and more narrow bottleneck for the structural biology: Recent empirical proteomics and genomic effort subject to automation of screening for crystallization conditions is successful in about 50% trials. The rest of the molecules are just abandoned. The structures of successfully crystallized molecules (often with unknown functions) go to the protein data banks - the "mineralogical collection" of the 21st century. On the other hand, a majority of the laboratories are trying to crystallize molecules of the known crucial functions.

The 7th International Conference on Crystallization of Biological Macromolecules (ICCBM7) in Spain, 1998 attracted ~ 230 participants, ICCBM8 in USA, 2000 ~ 320, ICCBM9 in Germany, 2002 ~ 420. There are 8 volumes of the Proceedings published as Special Issues of the well-recognized magazines - J.Crystal Growth and Acta Crystallographica D. Nevertheless, the biocrystallization is considered by non experts as a "kitchen," an attitude which was implicitly present in the NRC Report on the NASA Biocrystallography program. This is a mistake. This area should get a new impetus to faster, though, of course gradual, transformation from an art to science.

NASA has an exceptional position in the problem: the NASA biomacromolecular crystallization program brought about major recent progress in basic understanding of many phenomena and delivered a hint of Nature that the biomacromolecular crystallization may be more successful without convection. Making use of microgravity as one of the tools, these achievements should be developed further allowing the problem of biomacromolecular crystallization to be solved. This problem is a big stake in modern biological and materials science and technology and, in view of its scale and complexity, may be solved only on the National Level.

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NASA Program - 20 Years

- First publication – 1983
- The Program:
  - fundamentals: mainly terrestrial
  - empirical: "let us see" in space
- Results:
  - Fundamentals:
    - Same crystallization laws as for small molecules
    - New specifics:
      10 - 100 times larger species of complex shape to crystallize → slow growth, fragile crystals
      macromolecular surface easily changes, depending on solution composition, dirty solutions -> difficult to crystallize, disordered
    - self-purification in space hypothesis
  - Empirical:
    - 8000 experiments in space
    - ~20% of cases – improvements
    - no understanding why and when
- Strategies:
  - empirical continuation (NRC report, important proteins)
  - improvement of engineering, reproducibility
  - focused rational: why and when space may work -> rational design
  - balance needed

Statement of the Problem

To find out why and when crystals may grow more perfectly on earth and in space.

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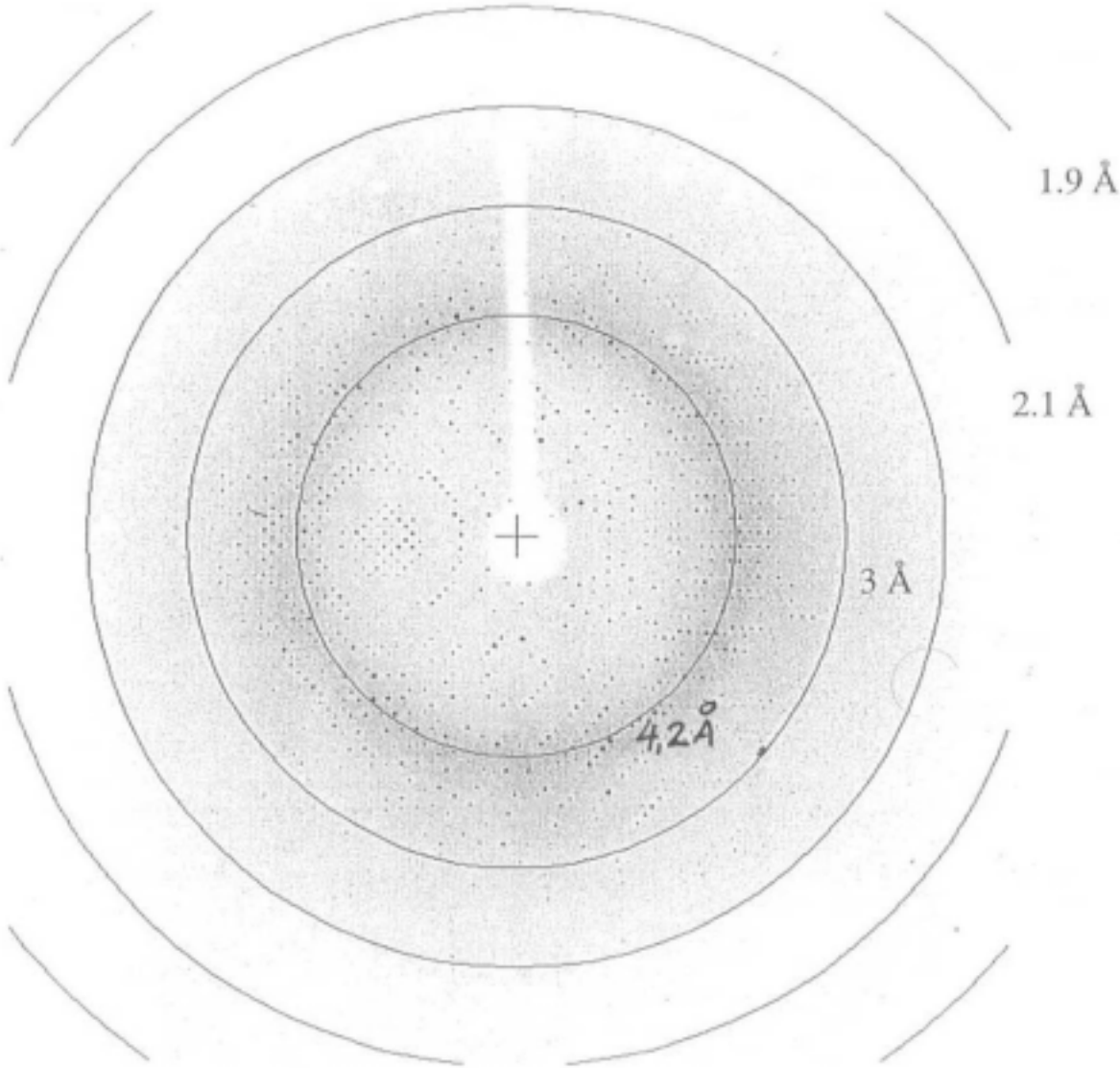
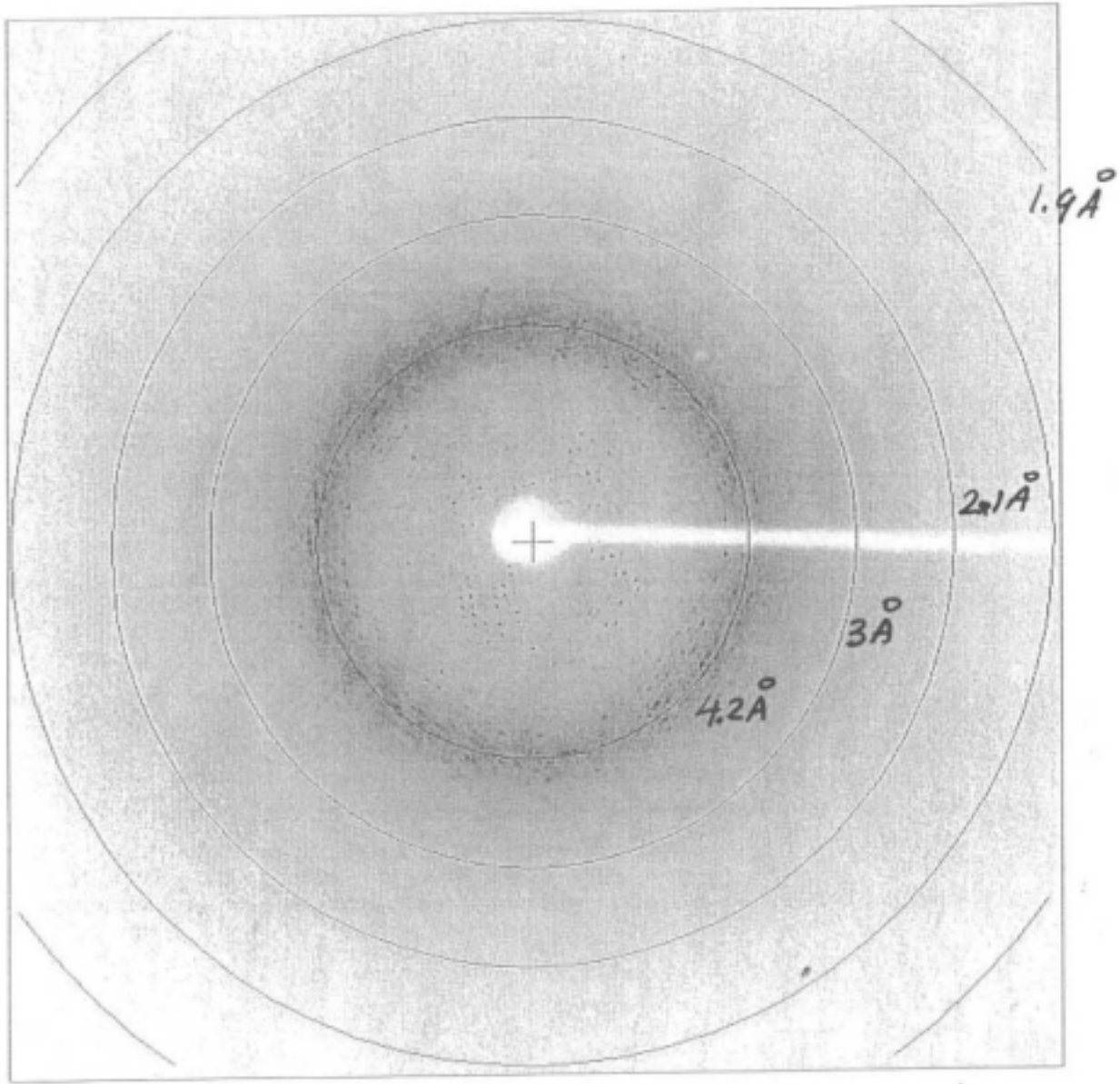




Apoferritin, M=450KDa, not purified
B.R. Thomas, Z. Hu.

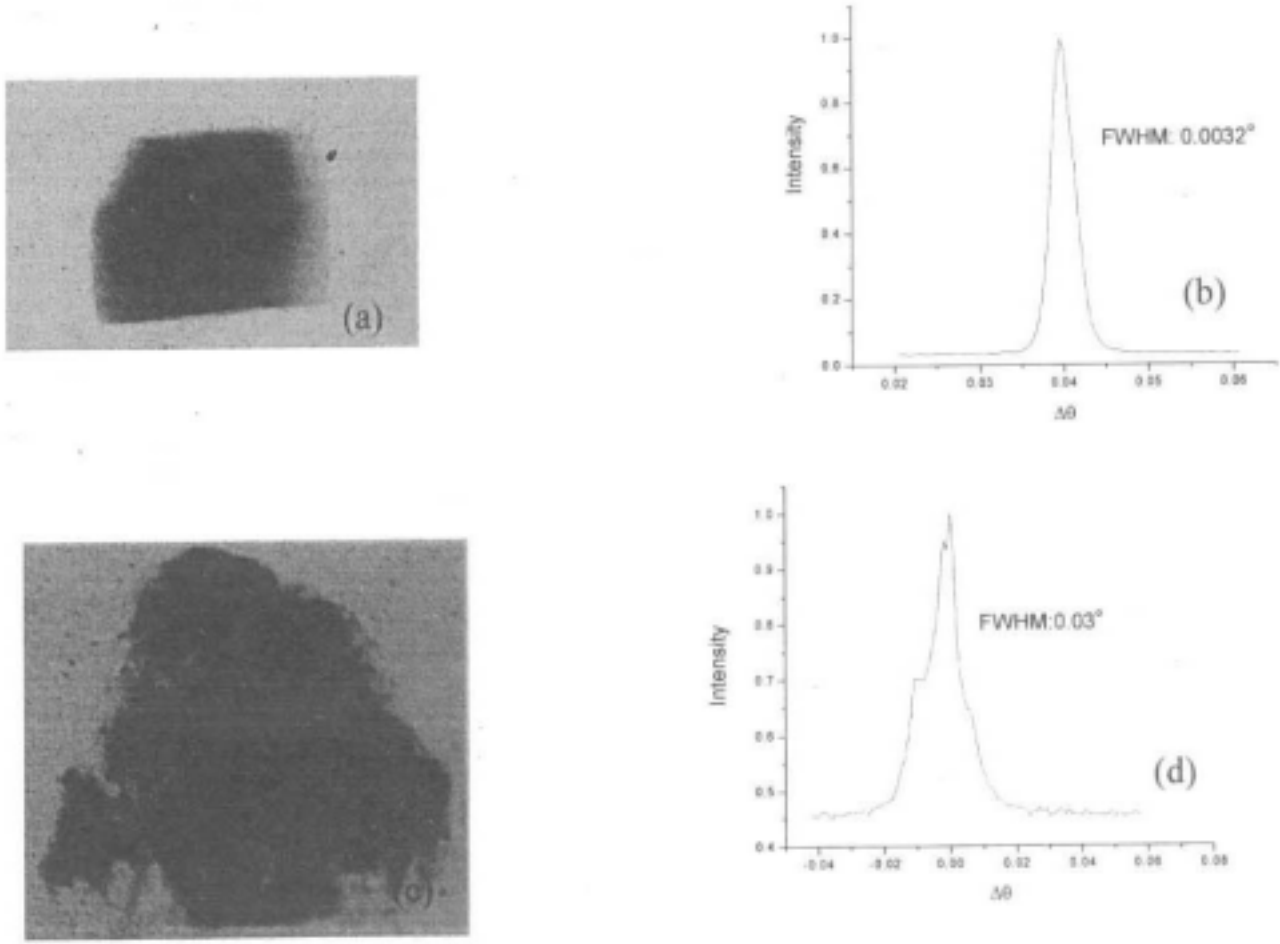
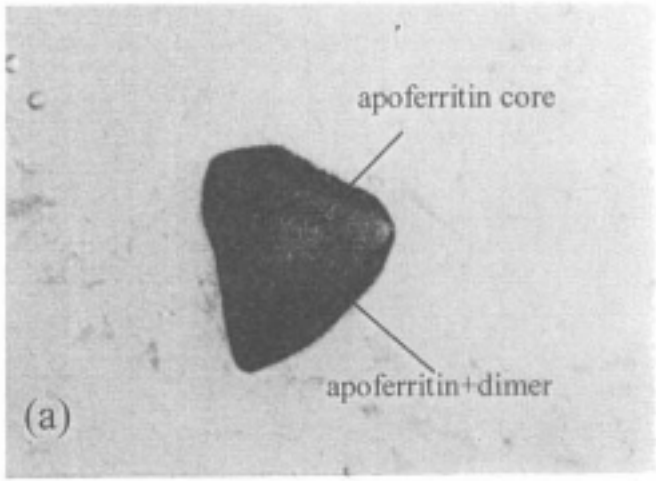
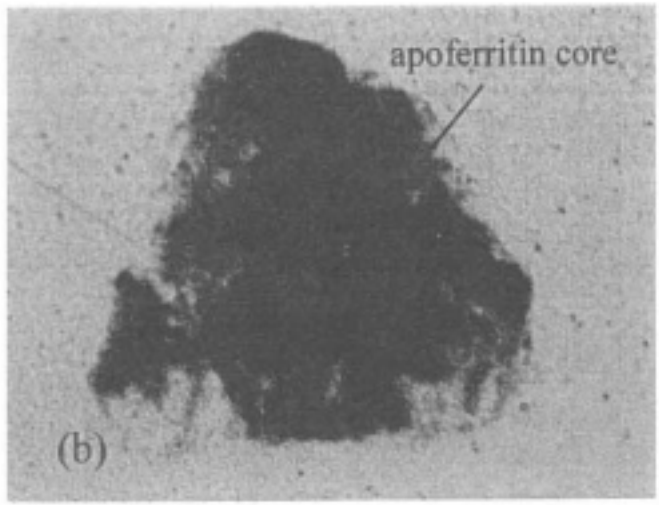


Fig. 2 Synchrotron x-ray topographic and mosaicity measurements of apoferritin and dimer-incorporated apoferritin crystals. (a) X-ray topograph of a crystal grown from gel showing uniform contrast across the sample (the white line at the bottom-left corner is an artifact), (b) a typical mosaicity measurement of apoferritin, (c) x-ray topograph of an apoferritin crystal incorporated with dimer after 4 days growth showing a highly mosaic structure, (d) a rocking curve corresponding to crystal c.





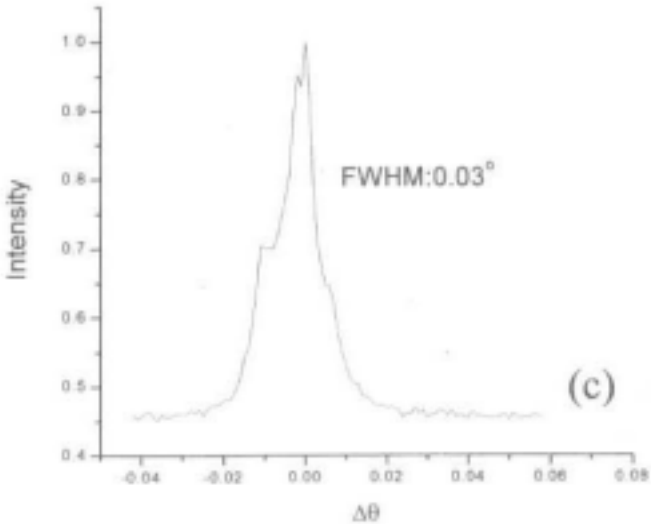
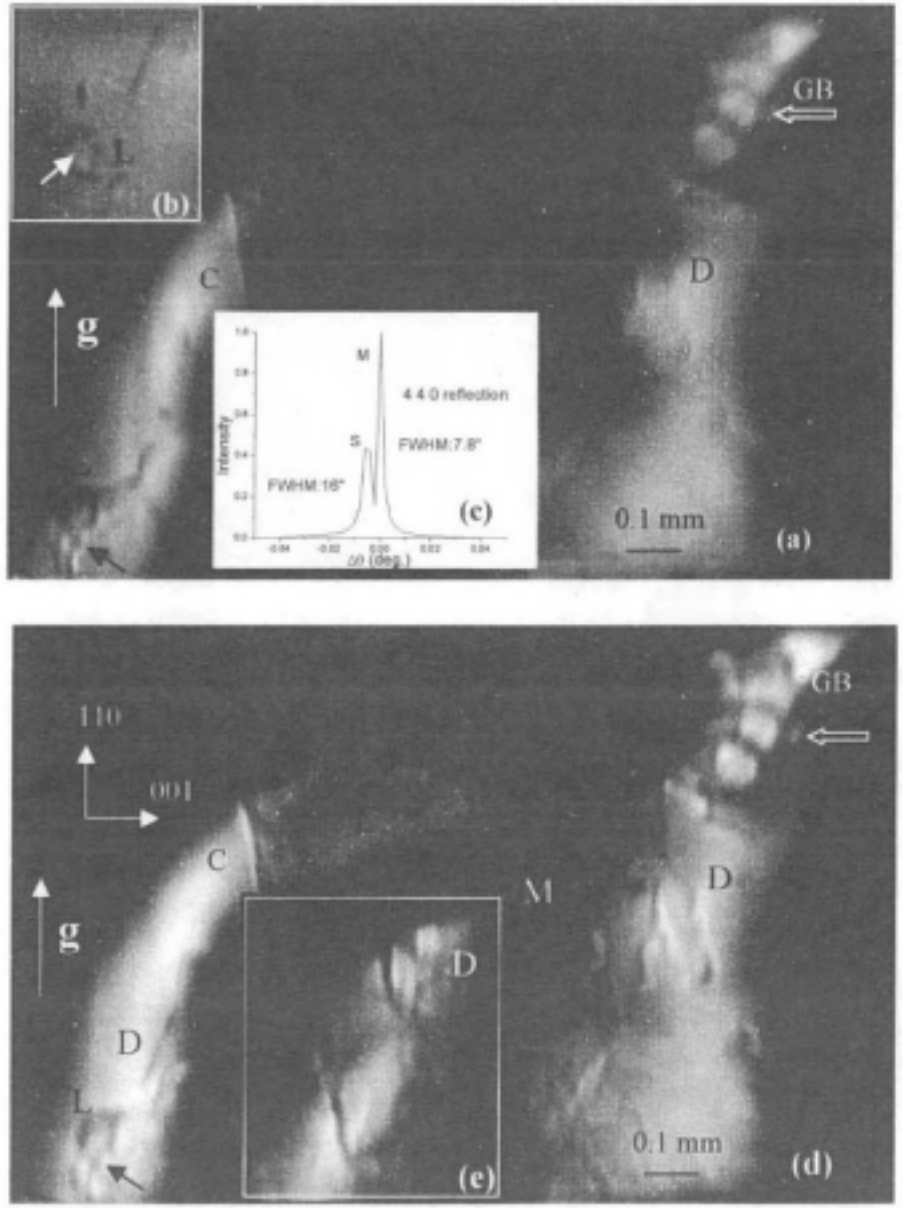


Fig. 1. One of apoferritin crystals with a high concentration of dimer added after 4-day growth. (a) Optical image showing a colorless apoferritin core and outer brown (apoferritin + dimer) crystal parts, (b) synchrotron x-ray topograph showing rather uniform diffraction contrast in the apoferritin core region and varying diffraction contrast in the outer (dimer+apoferritin) regions, (c) rocking curve.



Z. Hu ... Phys. Rev. Lett. 87 (2001), Oct 1

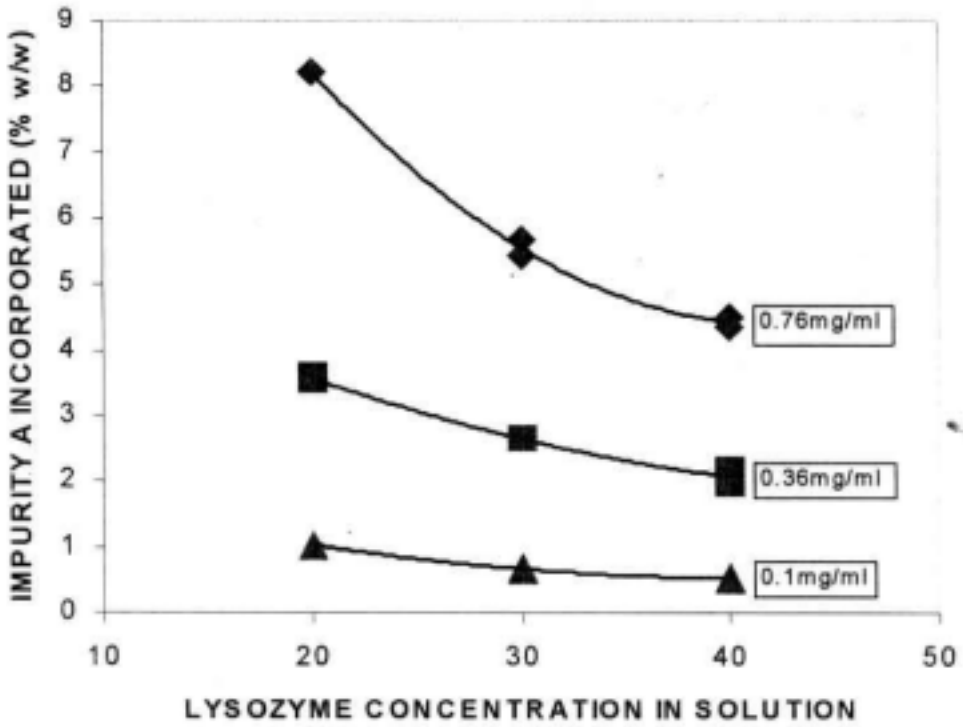
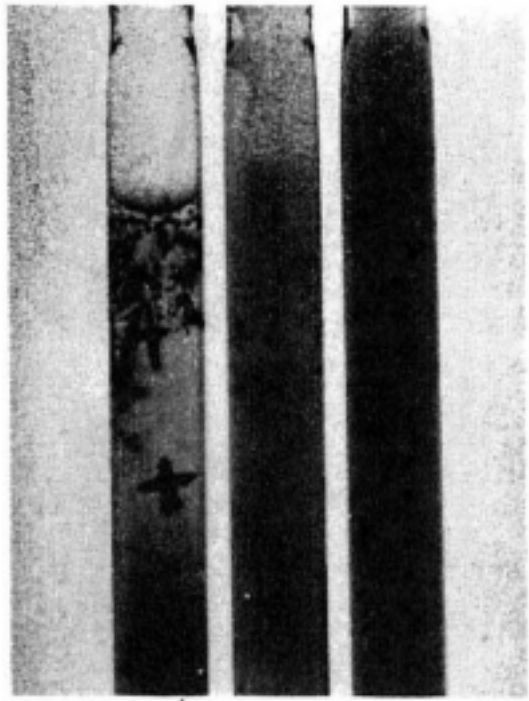


Fig. 6
Amount of acetylated lysozyme trapped by lysozyme crystals (C_{is}) as function of lysozyme concentration in solution (C_{pl}), for three different concentration (C_{il}) of acetylated species indicated at the curves. For each pair of C_{il} and C_{pl} two measurements are plotted.

All of this data is described by one distribution coefficient $K = 2.15 \pm 0.13$.

Apoferritin with pink-colored dimers.



crystals trap dimers | control – no crystals

Fig 2, Three cells similar to the ones shown in fig. 1. The right and the middle ones contain colored dimer and trimer impurity respectively but no crystals. Homogeneous distribution of these dimers stays in absence of crystals. When crystals appear in the left cell, they purify the solution, which becomes about colorless-impurity free, close to the crystals.

Chernov, Garcia-Ruiz, Thomas, J. Cr. Gr.
Proc. ICCBM8, 2001

Table 2. Distribution Coefficients of Impurities in Ferritin*

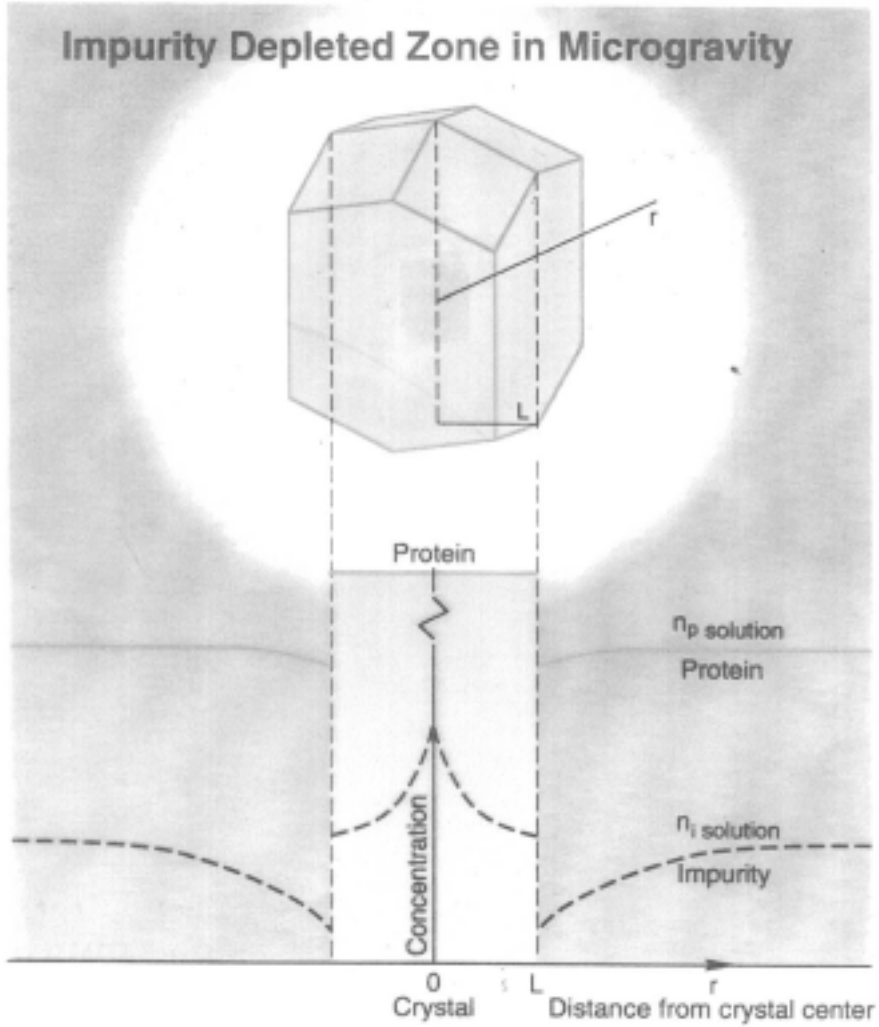
Monomer: pI = 4.0, Charge: (–) , Mr = 450 Kda. 24 Subunits, Mr = 19KDa
Solution: Ferritin –1mg/ml, NaAc – 0.2M, pH 5.0, $CdSO_4$ – 2.5% w/v
Impurity: Dimer 0.05 mg/ml (5% w/w), Others –10% w/w

Impurity, Mr(KDa), pI, Charge			Ground		Space	
			K	k	K	k
Dimer	900	4.2 –	4	$1.8 \cdot 10^{3}$	1.5	690
Ribonuclease	14	9.6 +	0.1	46	$<10^{-3}$	
Insulin	5.7	5.2 +	0.02	9.1	$<10^{-3}$	
Cytochrome C	13	10.6 +	0.02	9.1	$<10^{-3}$	
Myoglobin	17	7.0 +	0.006	2.74	$<10^{-3}$	
Ovalbumin	43	4.6 –	$<10^{-3}$		$<10^{-3}$	

$$K \equiv \frac{C_{iS}/C_{pS}}{C_{iL}/C_{pL}}, \qquad k \equiv \frac{C_{iS}/(g/cm^3)}{C_{iL}(g/cm^3)}, \qquad D\frac{\partial C_{iL}}{\partial n} = (k-1)VC_{iL},$$

* The volumetric distribution coefficients, k, are calculated from the measured K values making use of eq. (2) and $C_{pS}/C_{pL} = 457$ (Sec. 3.1).

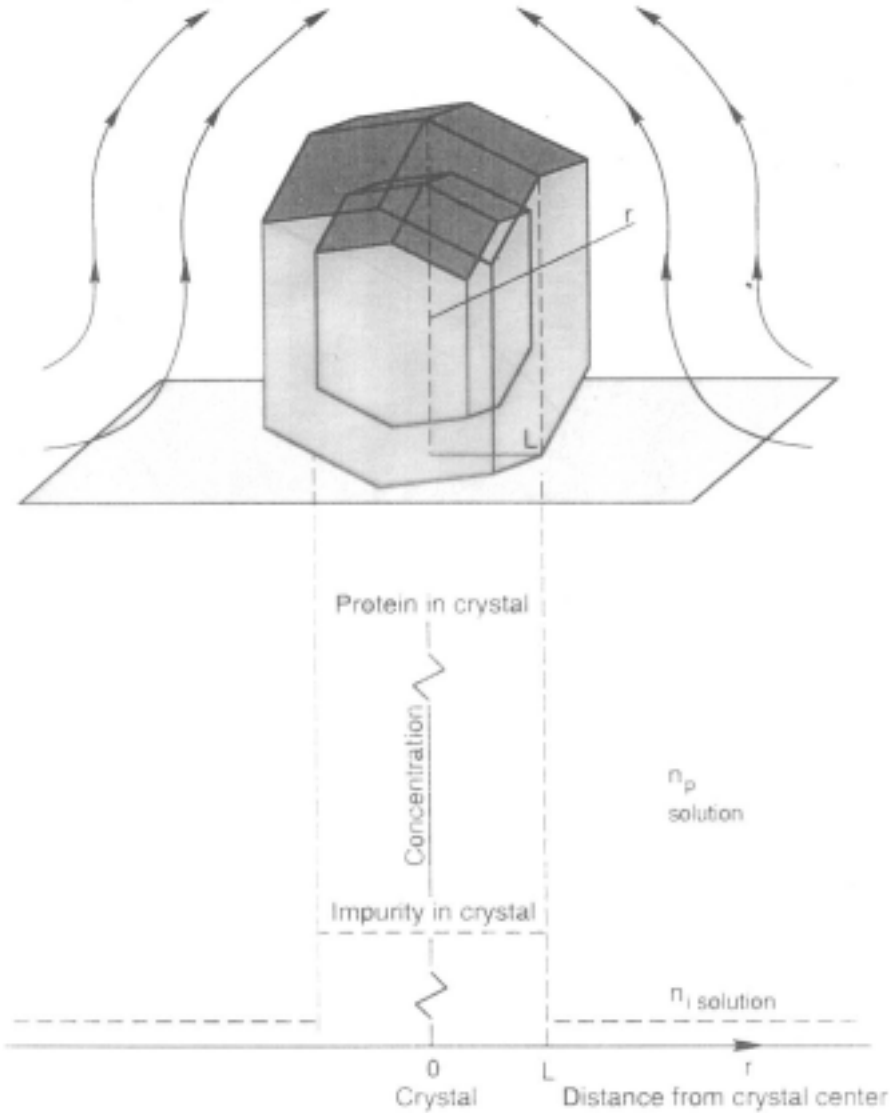
B.R. Thomas et al. J.Cryst. 2000

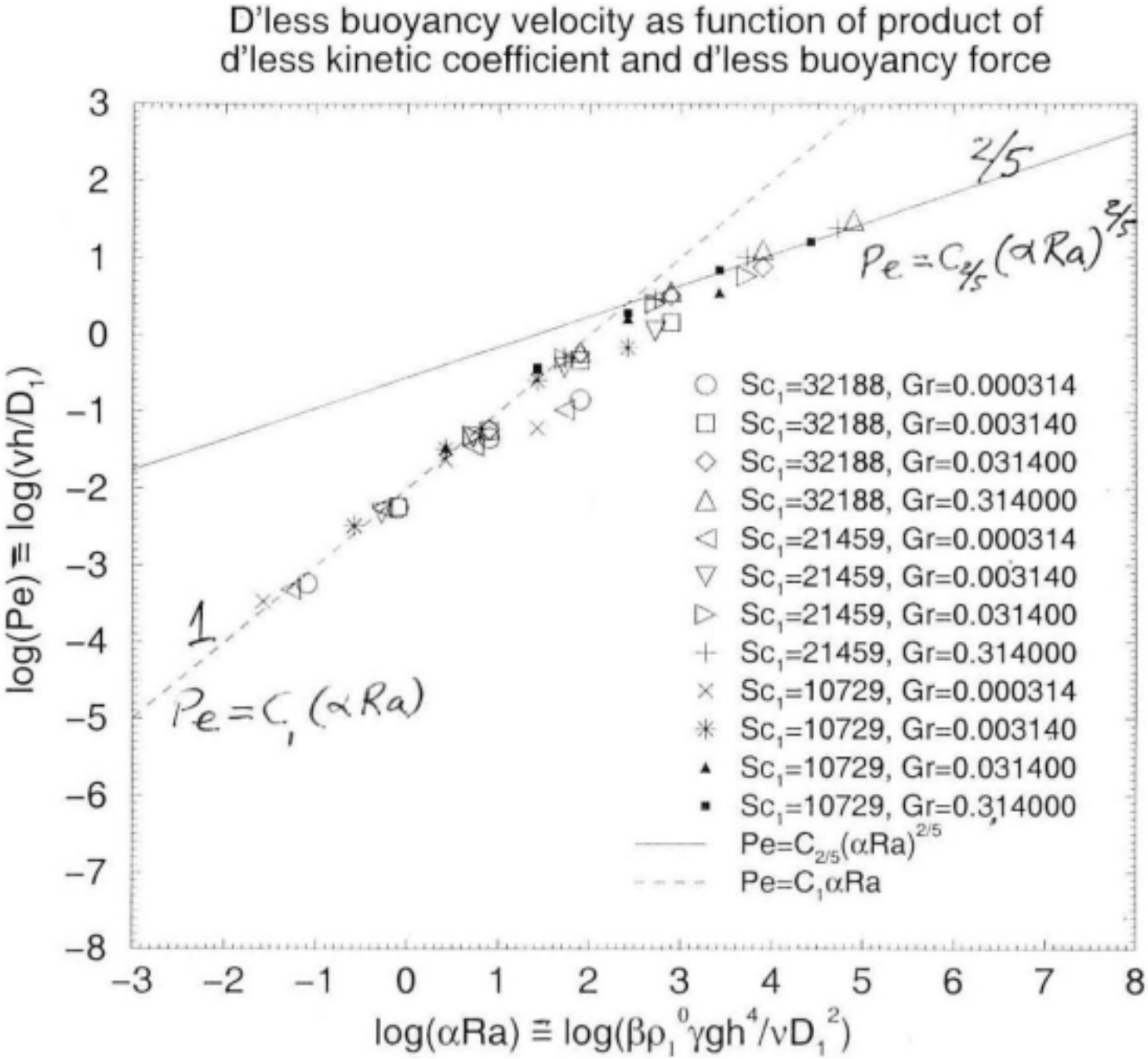


Distribution coefficient $$K = \frac{\left\langle \frac{n_i}{n_p} \right\rangle_{\text{crystal}}}{\left\langle \frac{n_i}{n_p} \right\rangle_{\text{solution}}}$$

Space: K = 2
Ground: K = 9

No Impurity Depleted Zone with Convection





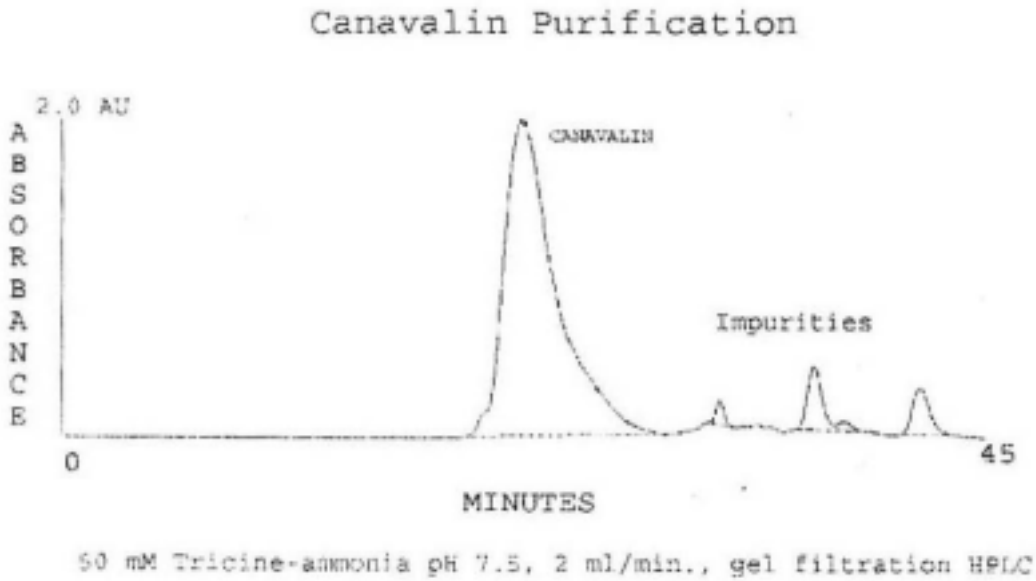
$$Sc_1 = \frac{\nu}{D_1}$$

$$Gr = \frac{\rho_1^0 \gamma g h^3}{\nu^2}$$

$$\alpha = \frac{\beta h}{D_1}$$

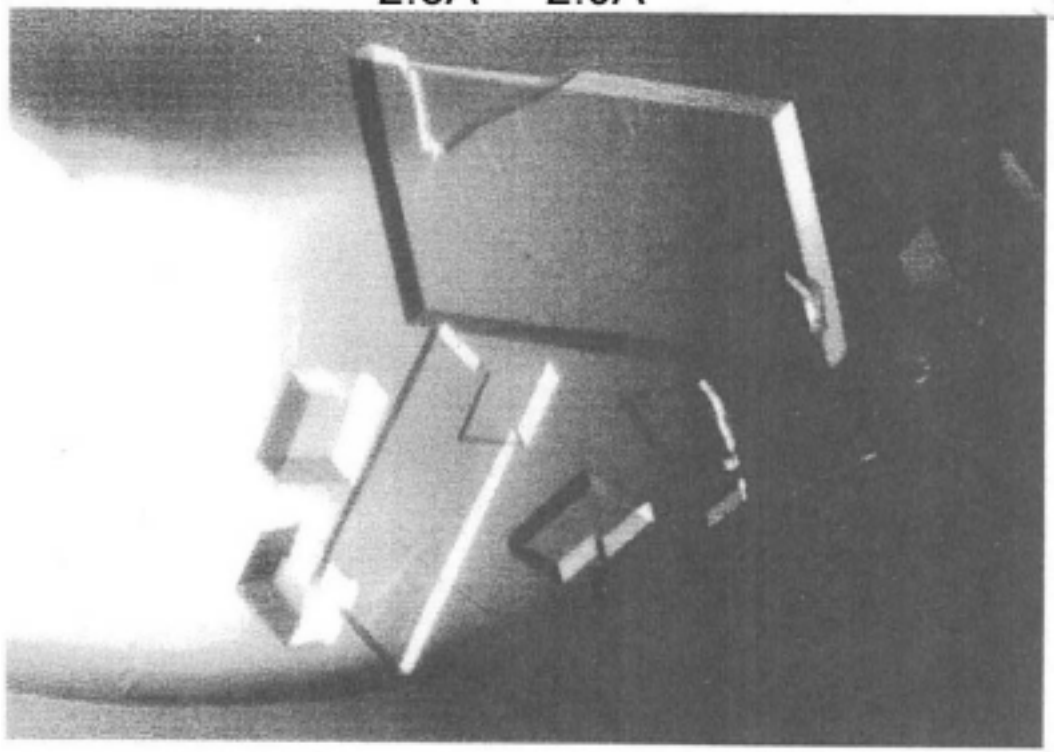
$$Ra = Sc_1 Gr$$

$$Pe = \frac{v h}{D_1}$$

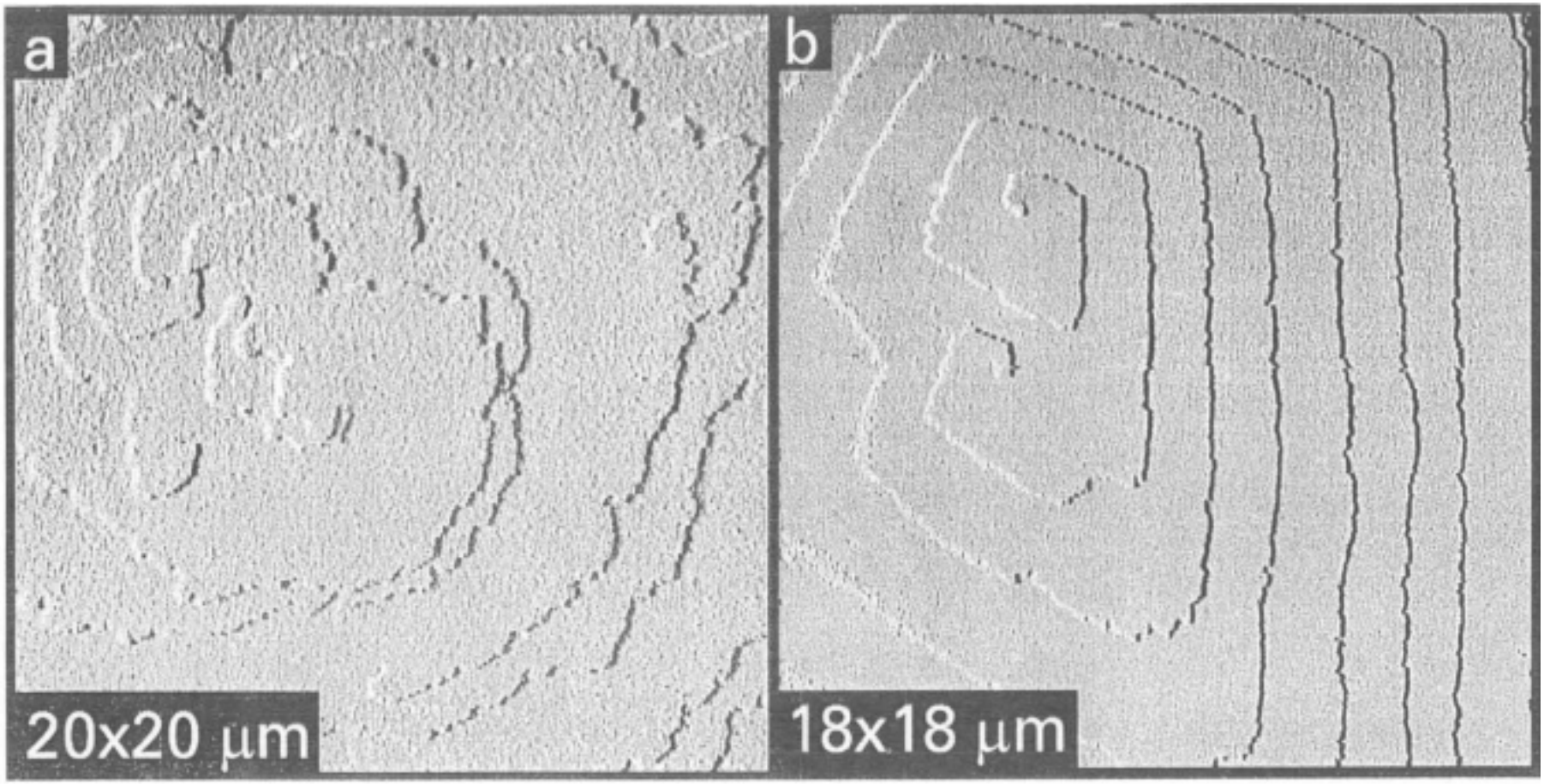


Canavalin
B.Thomas

2.6Å -> 2.0Å



Canavalin
B. Thomas



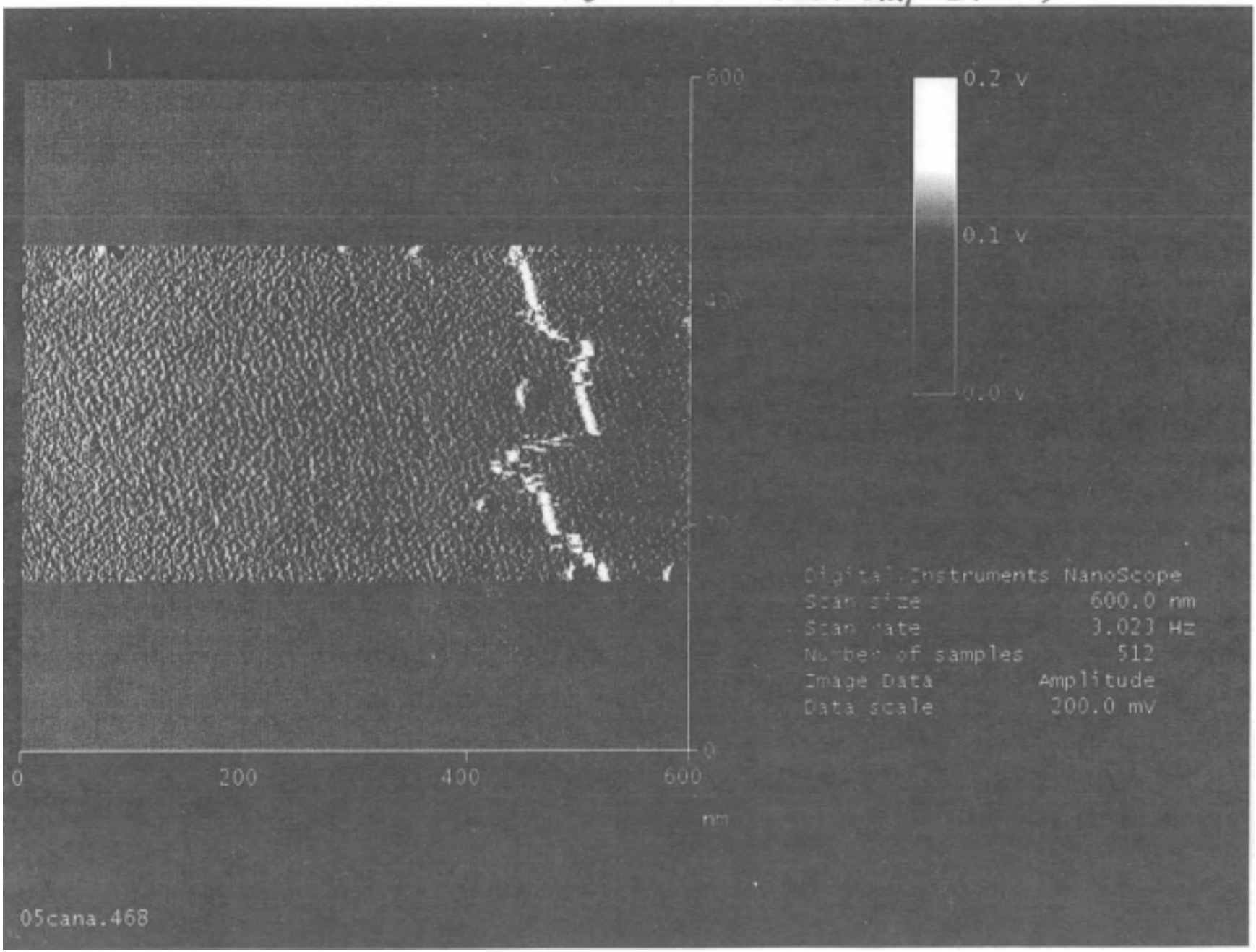
References: 1. A. A. Chernov, J. Cryst. Gr. 174 (1997) 354, Acta Crist A54 (1998) 859, J. Cryst. Gr. 196 (1999) 527; 2. B. R. Thomas, A. A. Chernov, P. G. Vekilov, D. C. Carter, J. Cryst. Gr. 211 (2000) 149

Canavalin

non-purified

purified

v (M. Plomp et al)



Abstract – Marc Pusey

New Directions in Biotechnology.

The macromolecule crystallization program within NASA is undergoing considerable pressure, particularly budgetary pressure. While it has shown some successes, they have not lived up to the expectations of others, and technological advances may rapidly overtake the natural advantages offered by crystallization in microgravity. Concomitant with the microgravity effort has been a research program to study the macromolecule crystallization process. It was believed that a better understanding of the process would lead to growth of improved crystals for X-ray diffraction studies. The results of the various research efforts have been impressive in improving our understanding of macromolecule crystallization, but have not led to any improved structures. Macromolecule crystallization for structure determination is "one of", the job being unique for every protein and finished once a structure is obtained. However, the knowledge gained is not lost, but instead lays the foundation for developments in new areas of biotechnology and nanotechnology. In this it is highly analogous to studies into small molecule crystallization, the results of which have led to our present day microelectronics-based society. We are conducting preliminary experiments into areas such as designed macromolecule crystals, macromolecule-inorganic hybrid structures, and macromolecule-based nanotechnology. In addition, our protein crystallization studies are now being directed more towards industrial and new approaches to membrane protein crystallization.

New Areas for Ground-Based Research

- Structural Genomics expressing and crystallizing proteins at a "wholesale" rate.
- Crystal growth physics studies cannot help structural genomics efforts, have not helped in "normal" crystal growth, and are not relevant to physiological protein-protein interactions.
- Can we make use of this body of information, and progress forward?

Yes, in areas such as:

- Industrial & pharmaceutical macromolecule crystallization
- Designed macromolecule crystals
- Macromolecule-inorganic hybrid structures
- Macromolecule-based nanotechnology
- New approaches to membrane protein crystallization

Industrial & Pharmaceutical

- A number of proteins are now produced as “industrial enzymes”,
  - Alpha amylase, lipases, as components of detergents
  - Lipases are used in organic syntheses
  - Xylose isomerase for processing of carbohydrates
  - Lysozyme as food additives.
- Crystallization is an important industrial purification process.
- The proteins are typically mutated to give specificity in activity, enhanced thermal or other stability, etc.
- Pharmaceutical proteins are often used in crystalline form (insulin)
- Dissolution properties are important, and are a designed in feature through modified crystal contacts, control of crystal size and size distribution
- We have now established contacts, with the goal of their leading to a formal working agreement, with NOVOzymes (Denmark), the worlds largest producer of industrial enzymes. We will study solubility, nucleation, crystal growth, and stability using their materials.

Designed Macromolecule Crystals

- Use molecular biology to design intermolecular contacts. Proteins are natural materials for use in this manner, offering facile manipulation at the genetic level to facilitate manipulation and modification at the product level.
- Defined contact pattern can give a correspondingly defined molecular pattern in three dimensions.
- Optically active and switchable elements on each molecule could be used to make the crystal a 3D optical memory device.
- Other modifications at the genetic or post genetic level can be used to build in (potentially) self assembling connection pathways between the molecules, leading to an electrical/optical read-write 3D optical memory device, with memory elements on the ca 5 to 50 nm scale.
- Self assembling biomaterials-based photovoltaic elements – use light harvesting proteins from plant photosynthetic systems to generate electrical currents, used as energy by other proteins.
- Highly speculative at this time, but likely to become a major area of research and development within 4-8 years. We are developing the protein canavalin as a model material for our preliminary work in this area.

Macromolecule-Inorganic Hybrid Structures

- **Combine the design flexibility of macromolecules with the electro-optical characteristics of nanoscale inorganic (or organic) materials.**
- **The use of nanomaterials is an emerging field, and bio-based hybrids can naturally co-develop with this.**
- **This lab seeks to make and characterize protein-quantum dot hybrid materials in partnership with members of the Materials group – preliminary work being funded by SD. Mutants of the protein canavalin have been generated by colleagues at UAH, and a first batch of CdSe quantum dots prepared by materials group. A Materials/Biotech. proposal has been submitted to NASA HQ, and a second Materials proposal to study canavalin crystal growth, *as a material*, is in preparation.**
- **Use of semiconductor materials may speed up development and increase the derived electro-optical materials versatility.**
- **Note that proteins have also been shown to have semiconductor properties.**
- **Quantum dots, metal – organic chelates (i.e., rubidium bipyridyl compounds), can serve as potential optical collectors or stimulated optical sources.**

New Approaches to Protein Crystallization

Soluble Proteins:

- **Lysozyme studies suggest the most important stage is the initial formation of a dimer, which can subsequently acquire greater symmetry and continue to grow into a crystal.**
- **This in turn suggests that for heretofore uncrystallizable proteins it may be useful to chemically crosslink them, forming a new species, from which to begin crystallization trials.**

Membrane Proteins:

- **Membrane proteins make up ~1/3 of the genome, but less than 0.5% of the structures solved so far. The major problem is getting them into solution, which has led to detergent-based and cubic lipid phase-based approaches to their crystallization, neither of which have been successful. We are now preparing Bacteriorhodopsin (halobacter) and Cytochrome C Oxidase (beef heart) as model / preliminary test membrane proteins.**
- **We are exploring novel solvent systems for use in solubilizing and crystallizing membrane proteins. Preliminary experiments with non membrane proteins show that proteins and common precipitation solutes are compatible with these solvents. An NIH grant proposal has been submitted.**

The Building Blocks of Materials: Gathering Knowledge at the Molecular Level

Dr. Sridhar Gorti / SD46

Two "start-up" positions were created within SD46 to pursue developments in the rapidly expanding areas of biomineralization and nano-technology. As envisioned by Dr. Sandor Lehoczy, the new laboratories to be developed must have the capacity to investigate not only processes associated with the self-assembly of molecules but also the examination of self-assembled structures. For these purposes, laboratories capable of performing the intended function, particularly light scattering spectroscopy and atomic force microscopy were created. What follows then are recent advances arising from the development of these new laboratories. With the implementation of the Atomic Force Microscopy Facility, examples of investigations that determine a correlation between the molecular structure of materials and their macroscopic physical properties are provided. In addition, examples of investigations with particular emphasis on the physical properties of protein crystals, at the molecular level, and subsequent macroscopic characteristics are as provided. Finally, progress in fabrication of technology at the nano-scale levels at the developmental stage is also presented.

Start-ups and Collaborations

- Startups and collaborations provide
  - continuity between old and new
  - expertise essential for NASA's missions
  - programmatic support for new technology development

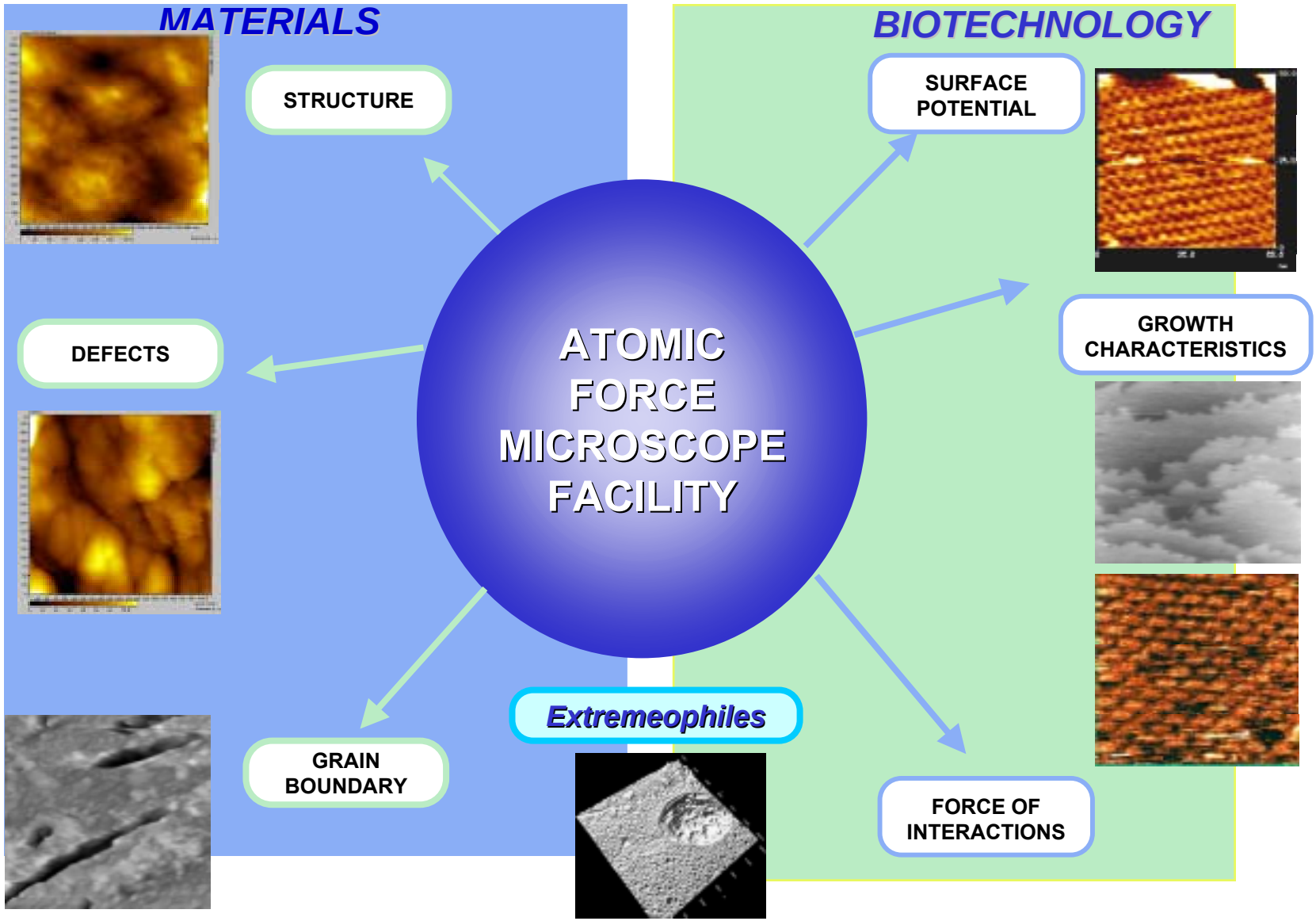
Visions for Startup

- Key Areas of Technological Development
  - Biomineralization
  - Nanotechnology
- Knowledge of the self-assembly of materials at the molecular level is critical
- Rely on expertise at Marshall
- Produce New Materials, Sensors, Etc.

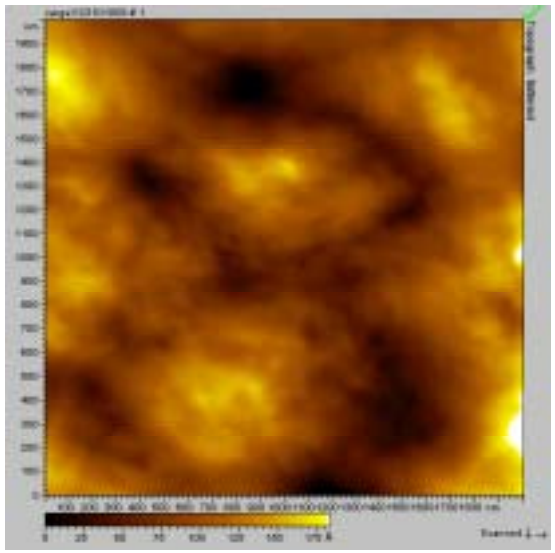
New Laboratories

- Light Scattering Spectroscopy (Dr. Phil Segre)
  - Investigate the physics and kinetics of self-assembly process *in situ*
- Atomic Force Microscopy (Dr. Sridhar Gorti)
  - Investigate topological and physical characteristics of self-assembled structures

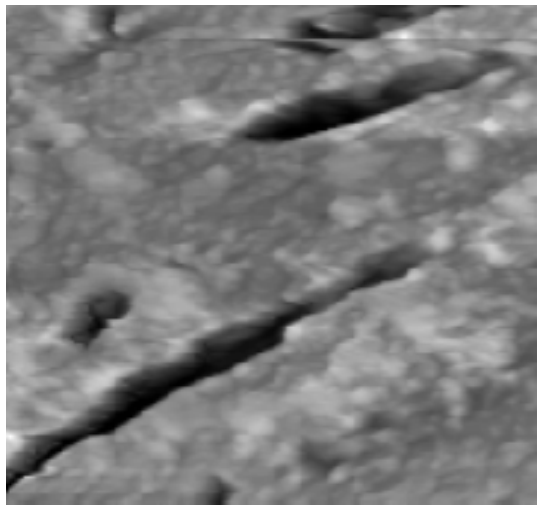
Atomic Force Microscopy



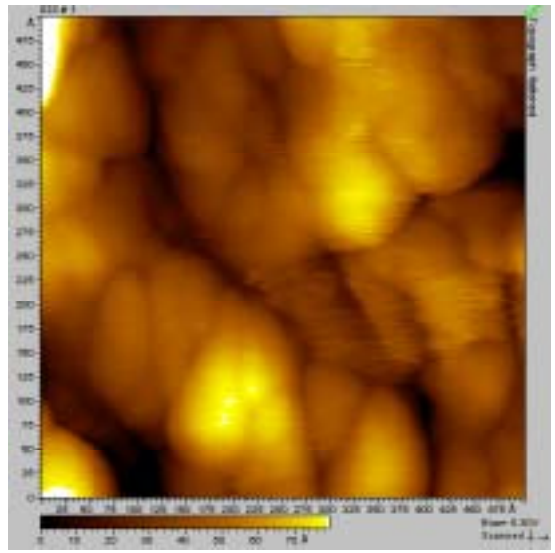
Materials Characterization



Carbon Aerogel

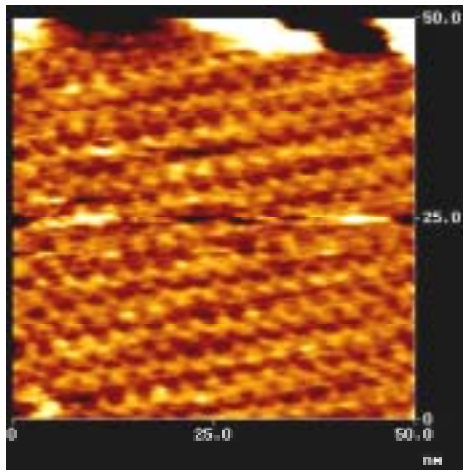


Copper Alloy

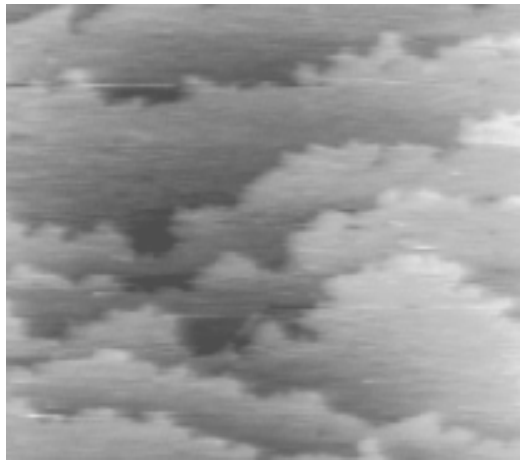


Copper Deposition

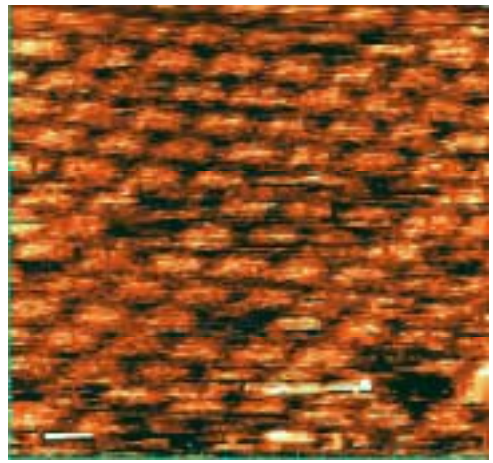
Physical and Biotechnology Research



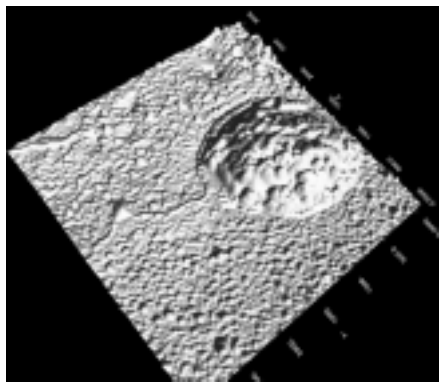
Lysozyme Surface



a-Amylase Surface



Glucose Isomerase

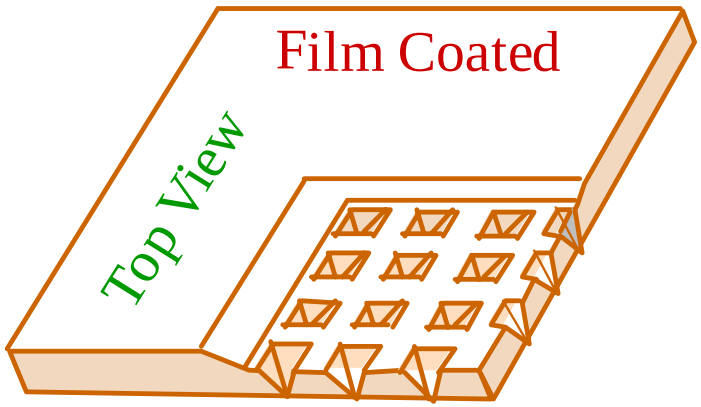


Extremophile

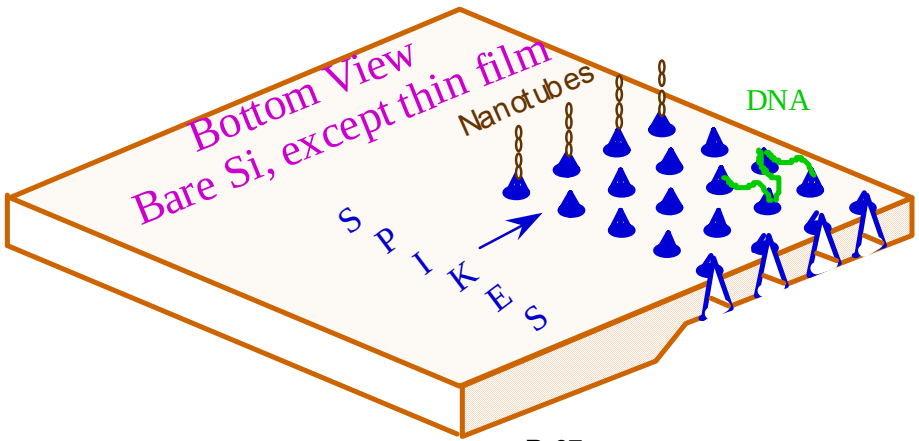
Nanotechnology

- **Fabrication**
  - Top-Down, assembly of molecules on Si-Devices
  - Bottom-up, manipulate individual atoms or molecules
- **Connectivity**
  - Remains as a major concern

A Possible Third Way



- Fabricate Si-Device
- Grow Carbon Nano-tubes (CVD)
- Align DNA Template
- Assemble Circuit



Multi-Disciplinary Efforts

- Si-Device Fabrication (Dr. Palmer Peters, Mr. Charles Sisk, Ms. Tia Ferguson)
- Connectivity, Switching (Engineering)
- Carbon Nano-tube Fabrication (Dr. Shen Zhu, Dr. Ching-Hua Su)
- DNA Template (Dr. Marc Pusey)
- Molecular Wiring

New Programs Utilizing Light Scattering and Flow Imaging Techniques for Macromolecular Crystal Growth and Fluid Dynamics Studies

Dr. Phil Segre, SD46

Dr. Phil Segre, a physicist by training, is a recent addition to the Biotech group, SD46, having joined NASA in August of 2000. Over the past two years I have been developing a laboratory for the study of macromolecular and protein crystal growth. The main apparatus for this work is a Dynamic Light Scattering apparatus, DLS, which is capable of making highly precise measurements of size distributions of both protein solutions and protein crystals. With Drs. Chernov and Thomas (USRA), I have begun a collaboration studying the affects of protein impurities on protein crystal growth and subsequent crystal quality. One of the hypothesis behind the differences between earth and space grown protein crystals is that the absorption of harmful impurities is reduced in space due to the absence of convective flows. Using DLS measurements we are examining crystal growth with varying amounts of impurities and testing whether there is a strong physical basis behind this hypothesis. With Dr. Joe Ng of UAH I have been collaborating on a project to examine the folding/unfolding dynamics of large RNA complexes. A detailed understanding of this process is necessary for the handling of RNA in biotech applications, and the DLS instrument gives details and results beyond that of other instruments. With Prof. Jim McClymer of the University of Maine (summer faculty visitor to NASA in 2001, 2002), we have been studying the crystallization process in model colloidal suspensions whose behavior in some cases can mimic that of much smaller protein solutions. An understanding of the self-assembly of colloids is the first step in the process of engineering novel materials for photonic and light switching applications. Finally I have begun an investigation into the physics of particle sedimentation. In addition to the DLS instrument I also have an instrument (called PIV) that can measure flow fields of fluids. The applications are to the dynamics of protein crystal motions both on earth and in low-gravity.

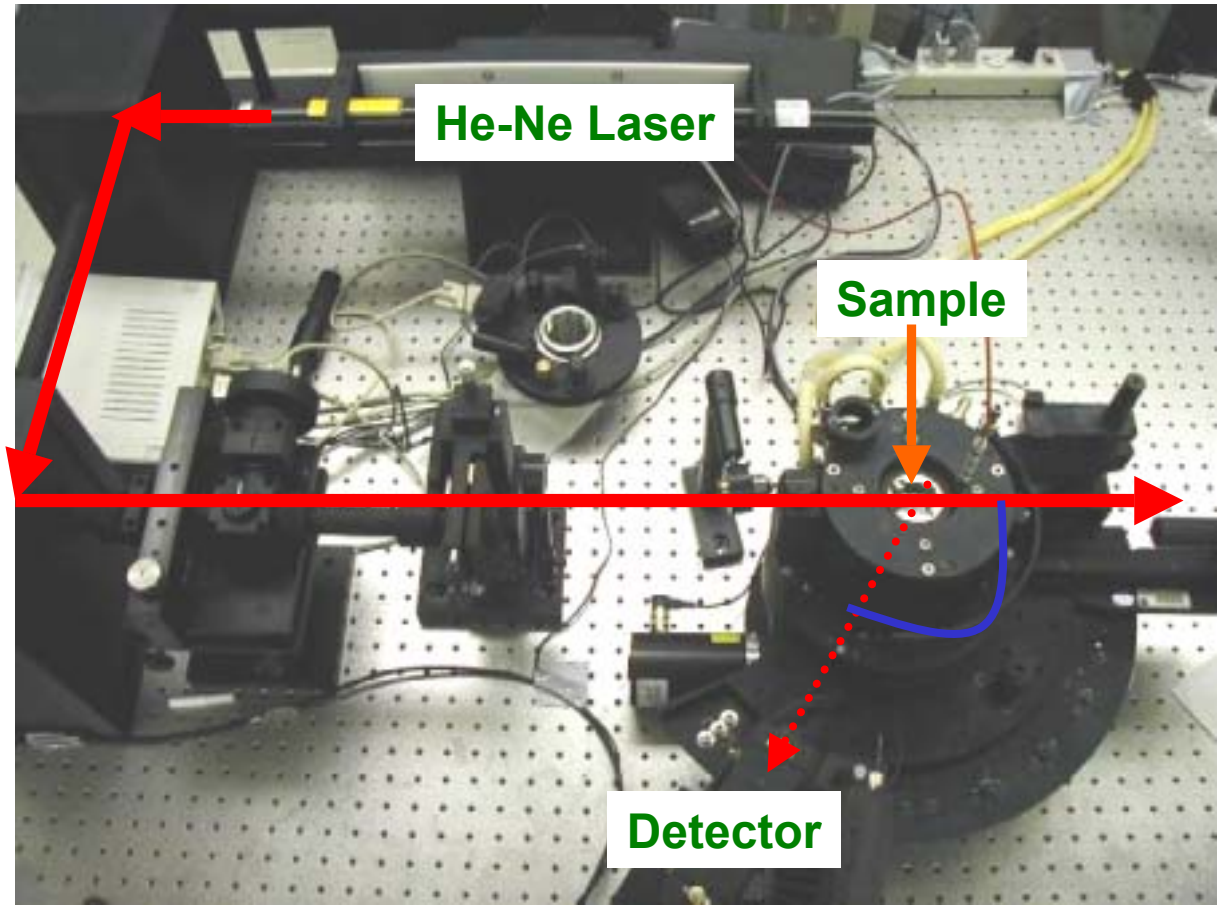
Dynamic Light Scattering Facility

Phil Segre, SD46.

Objective: Develop a physical understanding of protein crystal growth and the factors that affect crystal quality on the ground and in microgravity aboard the ISS.

- Effects of Solution Purity on Protein Crystal Growth
  (with Bill Thomas, Alex Chernov, USRA)
- Crystallization of Model Colloidal Suspensions
  (with Prof. Jim McClymer, Univ. of Maine)
- RNA Folding Transition
  (with Joe Ng, UAH)
- Pattern Formation during Particle Sedimentation

Dynamic Light Scattering Facility

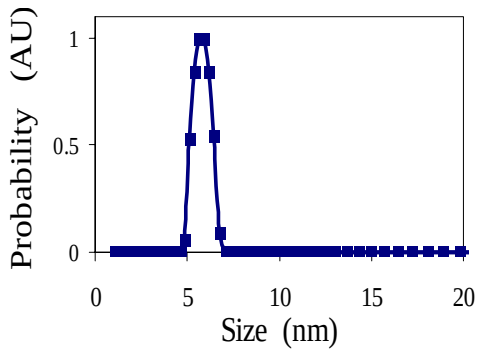


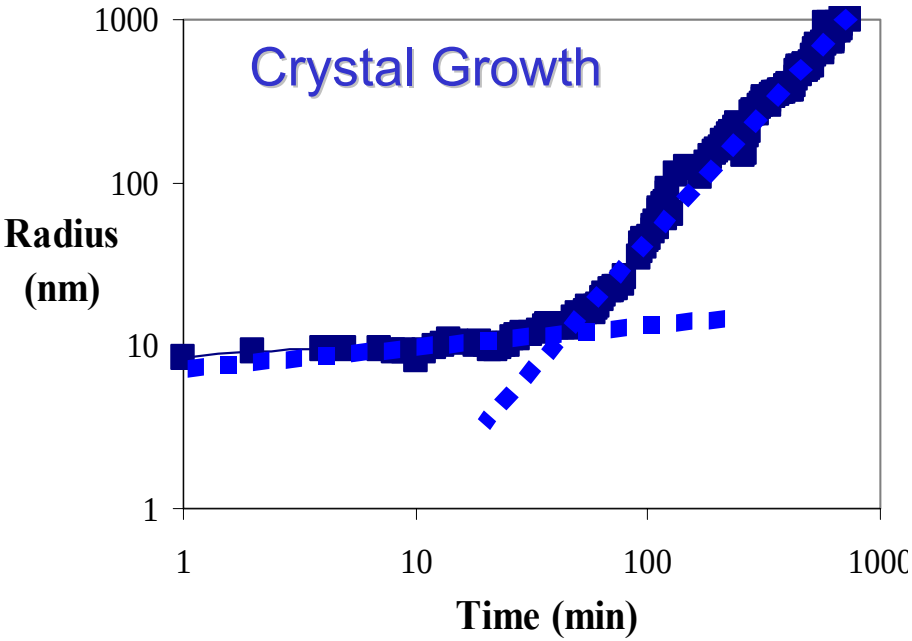
- General Facility for study of protein and macromolecular solution and crystal growth.
- Bldg. 4481/Rm. 404

Effects of Solution Purity on Protein Crystal Growth
(with Bill Thomas, Alex Chernov, USRA)

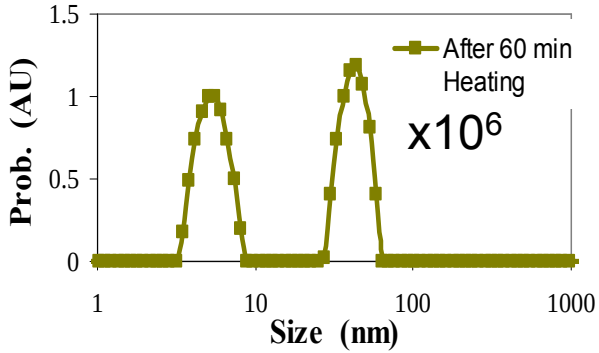
National Aeronautics and
Space Administration
George C. Marshall Space Flight Center

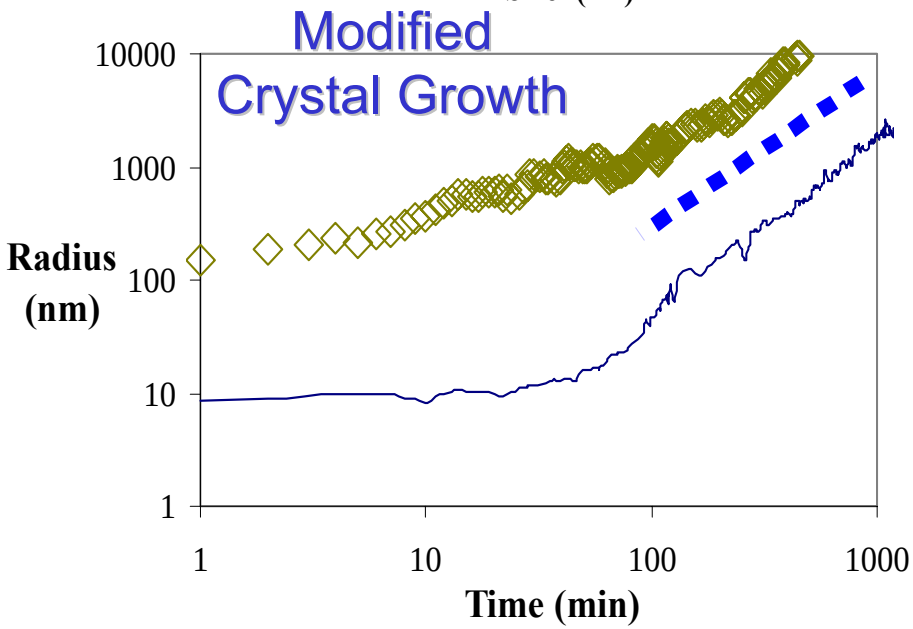
Crystal Growth from Highly Purified Solutions



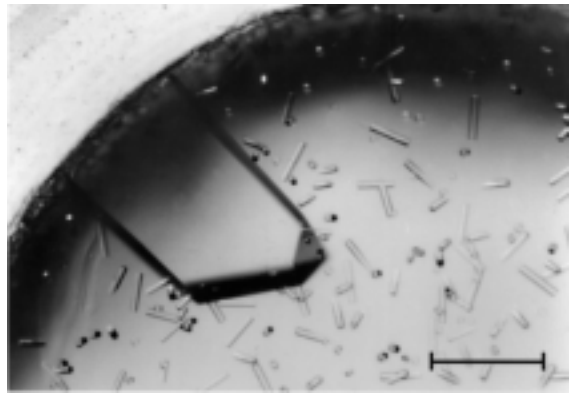


Crystal Growth from Solutions with **Impurities**





Effects of Solution Purity on Protein Crystal Growth
(with Bill Thomas, Alex Chernov, USRA)

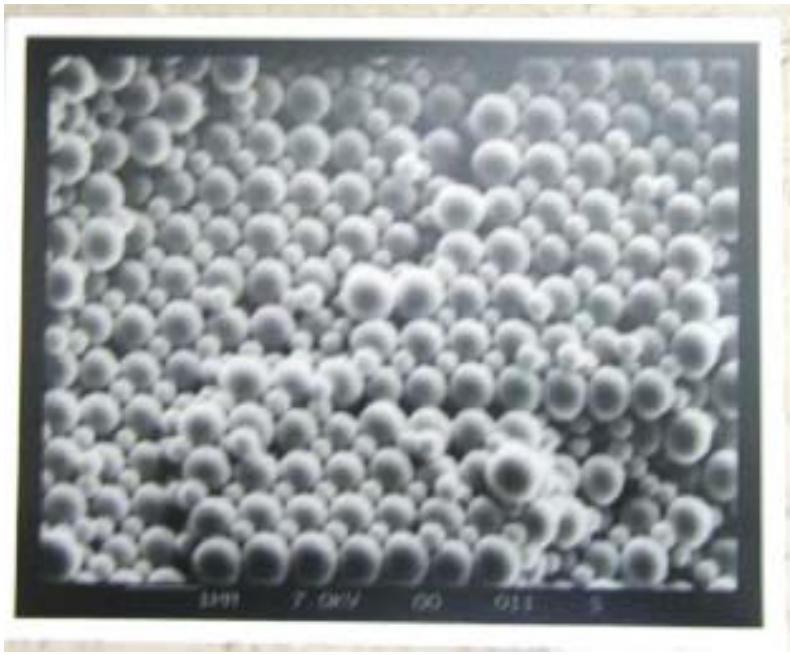


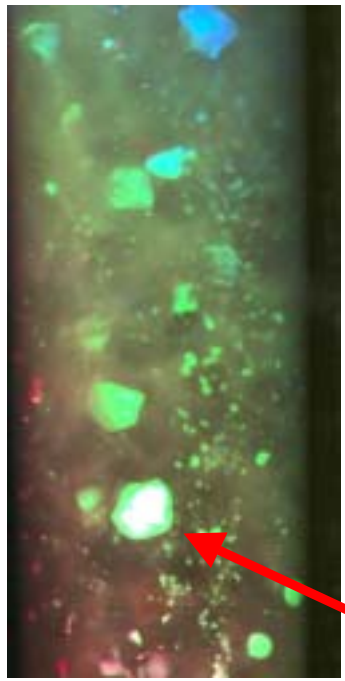
Objectives and Impact:

- Understand the role of protein impurities on crystal growth, crystal purity, and the structural information obtained. Are impurities a major cause of varied protein crystals on the ISS?
- Evaluate the impact of impurities to aid in the preparation of samples for the International Space Station.

Crystallization of Model Colloidal Suspensions
(with Prof. Jim McClymer, Univ. of Maine)

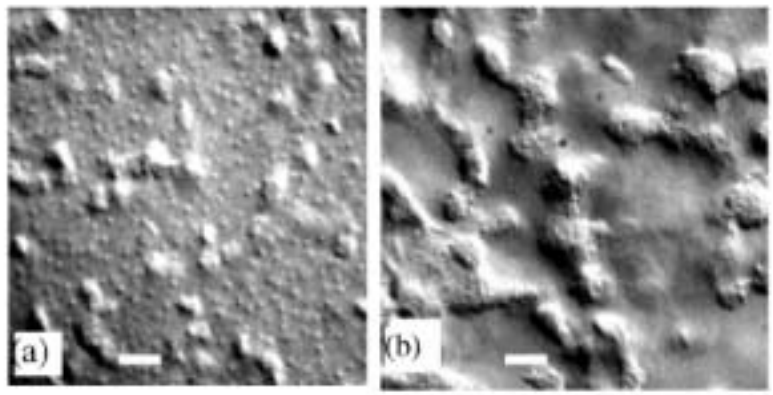
STM of Binary Colloidal Crystal.





Photograph of Binary Colloidal Crystals Aboard STS95.

Microscope Image of Fluid and Solid Phases of Aggregated Colloidal Suspensions.



Objectives and Impact:

- Understand the self assembly and crystal formation of model colloidal suspensions. Suspensions can serve as simpler models of more complex protein solutions. Colloidal Suspensions can in some cases be nearly density matched to the solvent so that the affects of fluid flow and sedimentation on crystal growth can be studied on the ground.
- Fabricate novel nano-materials for optic and photonic applications.
- Relevance to material science, biotech, and fluids.

V. Trappe, P. Segre et al., NATURE, Vol. 411, 14 June 2001, p. 772-775.

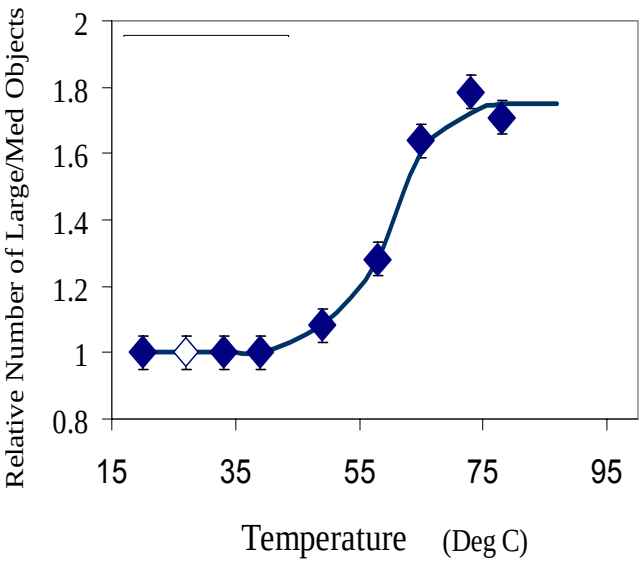
P. Segre et al, Physical Review Letters, 86, 25 June 2001, p. 6042-6046

RNA Folding Transition

(with Joe Ng, UAH)

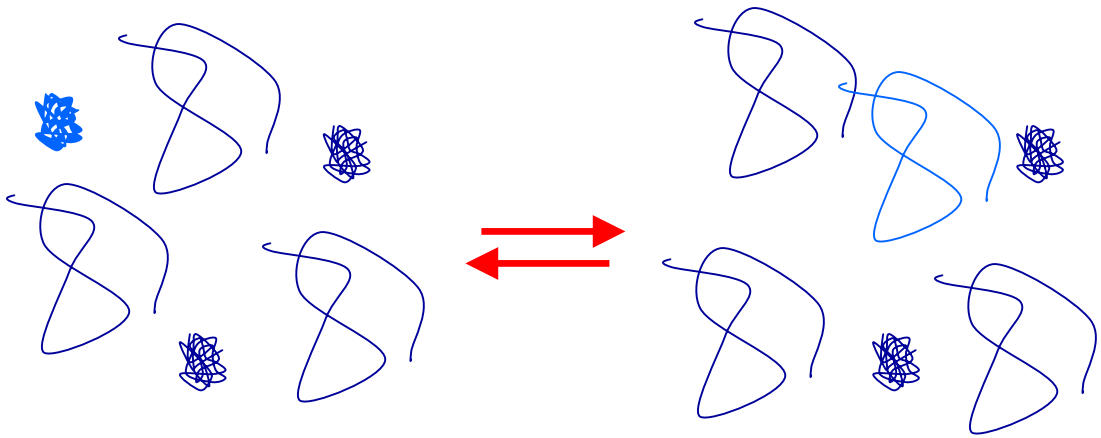
Objectives:

- **Understand the folding transition and the thermal behavior of large RNA molecules.**



T<<55 °C.

T>>55 °C.



An Observable Protein Crystal Growth Apparatus

Prof. Alex McPherson, UC -Irvine

To establish the physical processes that govern macromolecular crystal growth in microgravity .

Why:

- Establish the physical processes behind crystal growth in micro-gravity to aid in selection of biological crystals that most benefit from the micro-gravity environment.

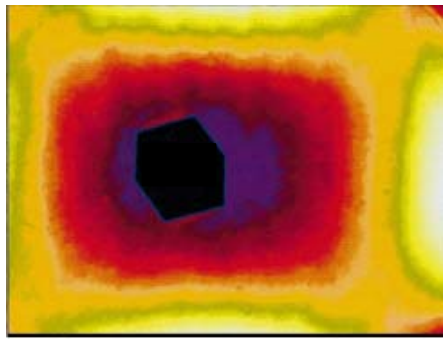
How:

- Measure and quantify concentration gradients around growing crystals and correlating their character with the quality of the resultant crystals.

Impact:

- To facilitate a more rational approach to the selection of protein samples whose crystals will benefit most from growth in micro -gravity, OPCGA will quantify the mechanisms of crystal growth and quality under a wide variety of sample conditions.

- OPCGA will benefit the biological community by providing a roadmap for obtaining optimal crystal diffraction and structural information in micro-gravity.



(L) OPCGA apparatus
(R) Protein concentration profiles

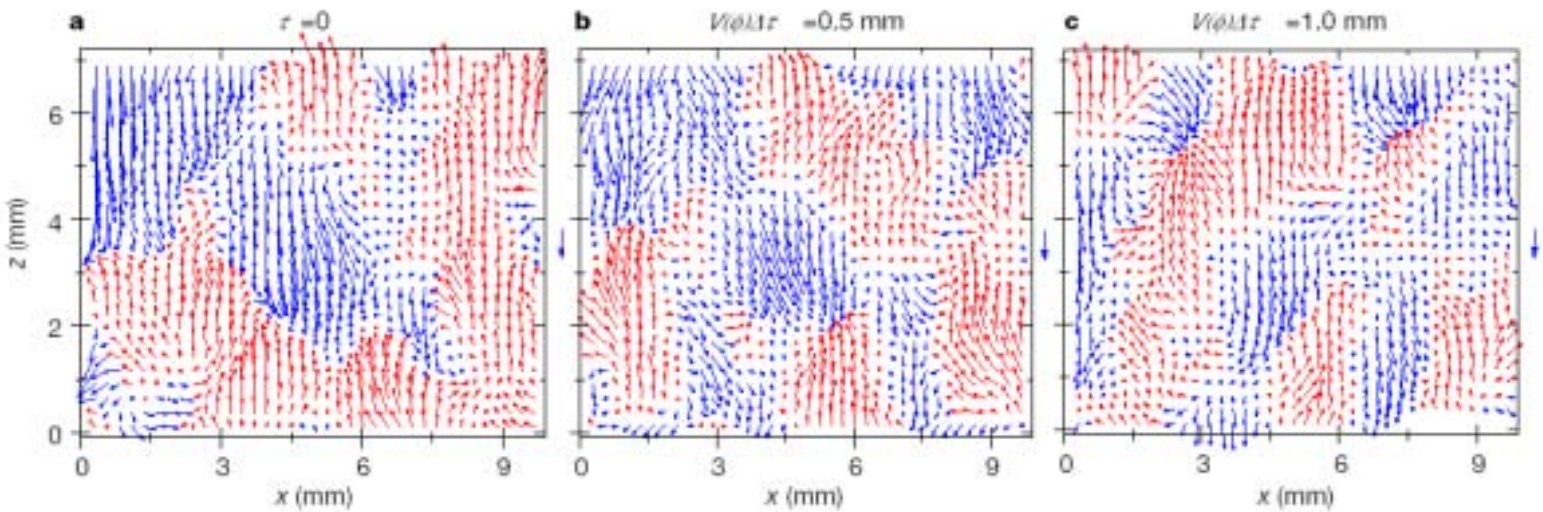
"*This team may be the only group currently engaged in realizing the necessary instrumentation for actually observing critical parameters of protein crystal growth in microgravity .*" NRA peer review, 1995

C22	Final Peer Review Date: 2001	Flight Hardware Availability : 2003

Pattern Formation during Particle Sedimentation

Objectives and Impact:

- **Understand the fundamental physics of pattern formation and fluid dynamics of particle sedimentation.**
- **Applications to flow in porous media, crystal sedimentation in low-g and 1-g.**



P. Segre et al, Physical Review Letters, 79, 29 September 1997, p. 2574-2577.

P. Segre et al., NATURE, Vol. 409, 1 February 2001, p. 594-597.

Biotechnology Protein Expression and Purification Facility

Dr. Laurel Karr

Abstract

The purpose of the Project Scientist Core Facility is to provide purified proteins, both recombinant and natural, to the Biotechnology Science Team Project Scientists and the NRA-Structural Biology Test Investigators. Having a core facility for this purpose obviates the need for each scientist to develop the necessary expertise and equipment for molecular biology, protein expression, and protein purification. Because of this, they are able to focus their energies as well as their funding on the crystallization and structure determination of their target proteins.

Biotechnology Protein Expression and Purification Facility

- Dr. Laurel Karr
- Core Facility Science Lead

Project Scientist Core Support Facility - Description

The core facility provides molecular biology, protein expression, and protein purification capabilities in support of Biotechnology Science Team Project Scientists and NRA – Structural Biology Test Investigators. This facility eliminates the need for similar equipment and expertise in every laboratory.

Project Scientist Core Support Facility - Personnel

• Dr. Laurel Karr	Core Facility Science Lead
• Christine Malone	Lab management, Molecular Biology
• Rebecca Miller	Fermentation
• Blake Moore	Protein Purification
• Melissa Burk	Molecular Biology, Fermentation, Protein Purification
• Dr. Young Hong	Molecular Biology, Fermentation, Protein Purification

Project Scientist Core Support Facility – Project Prioritization

1. Projects that support both an NRA - Structural Biology Test Investigation and the Project Scientist for that investigation.
2. Projects that support a Project Scientist, but not a Structural Biology Test Investigation.
3. Projects that support an investigator at MSFC who is not a Project Scientist.

- Note: Every project must have a Memorandum of Understanding.

Ground Experiments

	Protein	mgs
DCPCG (Malone	glucose isomerase	220
	equine serum albu	2700
	B-amylase	522
	a-chymotrypsinoge	3850
	concanavalin A	360
	catalase	500
Kundrot	bFGF	120
	thaumatin	1886
	thaumatin I	299
	thaumatin II	68
van der Woerd	GFP	187
Sumida	GFP	284
Achari	tNOX	2500
	cleaved tNOX	72
	GFP	101
Kirkland	canavalin	3000
Pusey	tNOX	136
Holmes	GFP	16
Ferree	ESA	130
Moore	ESA	88
	ESA dimer	31
	RPA 14/32	4
Adamek/Moore	tNOX	32
Borgstahl	RPA 14/32	91

Flight Experiments

		Investigator	Protein
ISS-2A	EGN	van der Woerd	GFP
STS-97	EGN	Pusey	GFP
ISS-5A	EGN	Kundrot	thaumatin
ISS-5A	EGN	Achari	tNOX
ISS-5A	EGN	Karr/Malone	HBAP
ISS-5A	EGN	van der Woerd	GFP
ISS-6A	PCAM	Achari	GFP
ISS-6A	PCAM	Kundrot	bFGF
Flight UF-1	PCAM	Kundrot	bFGF
Flight UF-1	PCAM	Achari	GFP
Flight UF-1	PCAM	Kundrot	thaumatin

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December-2003

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14. ABSTRACT

Documentation of the internal science research at the Biological and Physical Space Research Laboratory as presented in a review to Dr. Ann Whitaker, MSFC Science Director, in July 2002. These presentations have been revised and updated as appropriate for this report. The report documents flight and ground experiments in microgravity materials science and biotechnology science and space radiation. All of the work described includes significant scientific contributions by internal scientists (usually as principal or co-investigator on the research grant). Much of the research is in collaboration with external scientists. All the funding was provided as the result of competitive proposals evaluated by internal or external peer review processes. The external flight and ground research that our laboratory supports for the NASA program will be reviewed in a separate report.

15. SUBJECT TERMS
materials science, microgravity research, biotechnology, science for space exploration.

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