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Center for Advanced Materials

**CAM**

**RESEARCH NOTES**

Volume 1 Number 2

August 1987

INSIDE . . .

*Industry-Laboratory exchange program brings total of five industrial fellows to CAM in FY87*

*Novel optical techniques allow study of polymerization of molecular monolayers*

*Viscosity anomalies in liquid crystalline polymers explained at molecular level*

*NMR probe developed to allow real-time observation of catalyst reactions*

*First direct microscale mapping of carbon in GaAs*

*Gene for materials synthesis enzyme cloned and expressed in yeast*

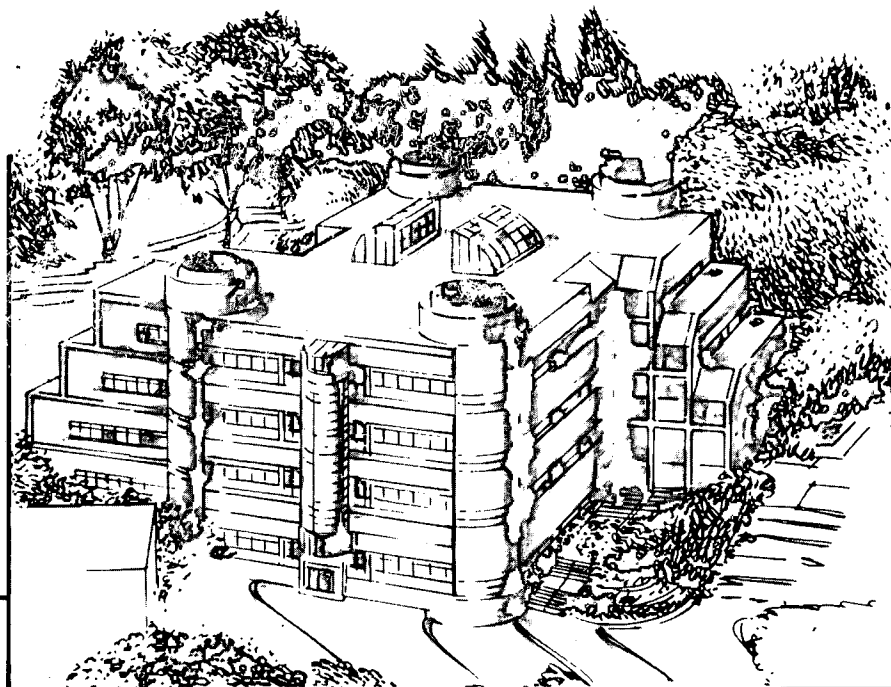
*Al-Li alloys show unexpected crack growth rates*

*Delamination of ceramic-metal interfaces reduced through energy absorption by metal layer*

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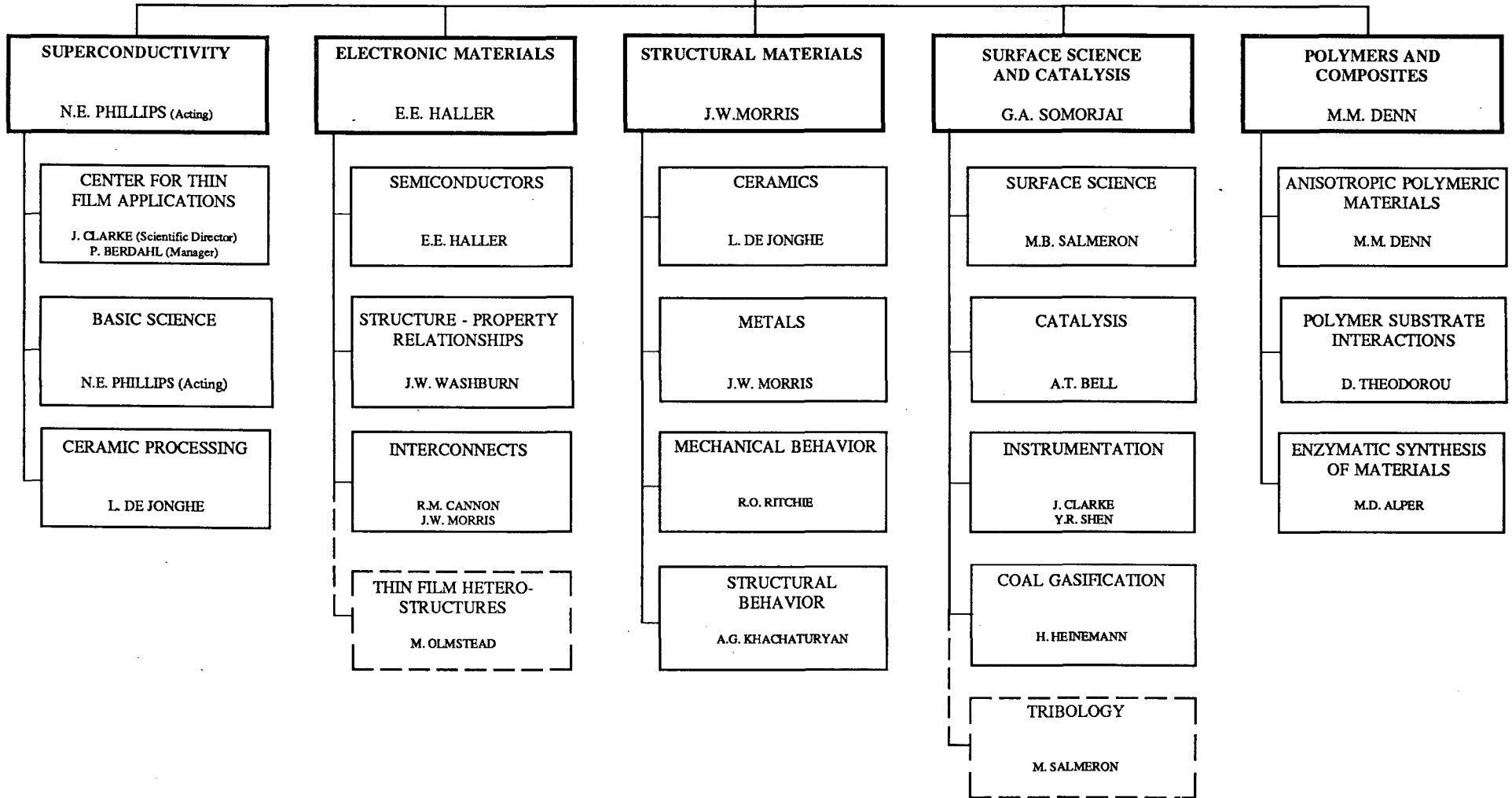
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# CENTER FOR ADVANCED MATERIALS

**Research Notes** is published three times each year by the Center for Advanced Materials at Lawrence Berkeley Laboratory. It is distributed widely in the U.S. materials-dependent industrial community and is one mechanism by which recent research results at the Center are communicated to that audience. More detailed information about this and related research can be found in the references cited on each page. The CAM scientists involved can also be reached at the telephone numbers listed.

The Center for Advanced Materials was established in 1983 and receives major funding from the U.S. Department of Energy, Office of Basic Energy Science. Its mission is to perform basic research in areas of materials science of importance to U.S. industry. We welcome communication from any industrial research groups interested in collaborations or other interactions with the CAM programs.

**CENTER FOR ADVANCED MATERIALS**  
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R.O. RITCHIE  
**ASSOCIATE DIRECTOR**  
M.D. ALPER



## INDUSTRY PARTICIPATION

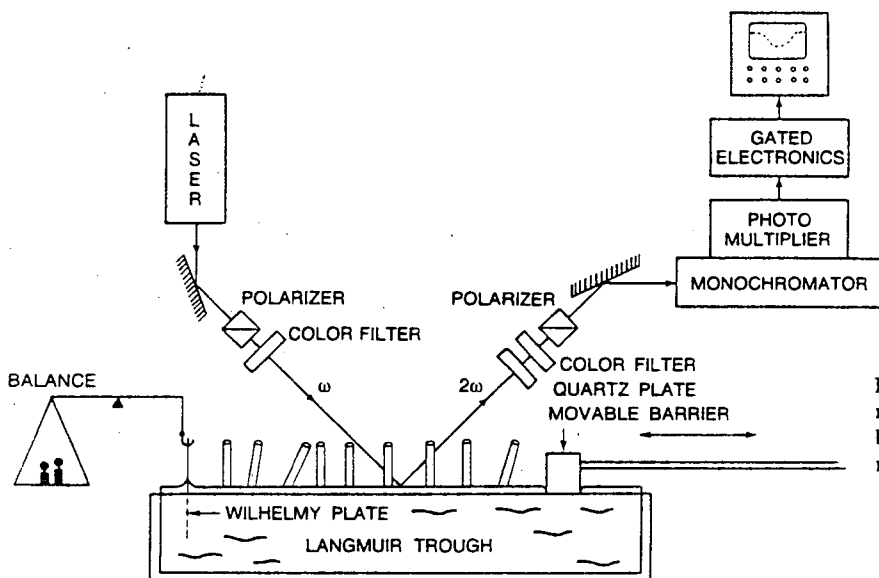
### INDUSTRY-LABORATORY EXCHANGE PROGRAM BRINGS TOTAL OF FIVE INDUSTRIAL FELLOWS TO CAM IN FY87

Three more CAM programs have awarded Industrial Fellowships to senior industrial scientists. The Fellows work at CAM for as long as one year, coupling their industrial experience to the basic experimental and theoretical research capabilities of CAM scientists. This brings to five the number of such Fellows this year, all of whom are also participants in DOE's Industry-Laboratory Technology Exchange Program which provides support for their visits.

A. V. Ramamurthy, Senior Research and Development Scientist at Union Carbide holds patents for polymer processing techniques involving polymer-metal interactions. He is working with the Polymers and Composites Program which is seeking to develop an understanding of the molecular basis for these interactions.

Mahn Won Kim, Senior Staff Physicist at Exxon Research and Engineering Company is pursuing industrial applications of the second harmonic generation techniques developed at the CAM Instrumentation Program. These allow studies of the structure of surfactant monolayers at water interfaces.

Dr. David L. Bliss is Engineering Manager for Gallium Arsenide Materials at M/A-COM Advanced Semiconductor Operations, a leading U.S. vendor of semi-insulating GaAs. He will bring his experience with the problems of industrial scale-up of crystal growth to the CAM Electronic Materials Program which has developed new crystal growth technology and characterization techniques.



Experimental apparatus for SHG from molecular monolayers on water. Movable barrier changes the surface area; balance measures the surface tension.

**INSTRUMENTATION FOR SURFACE SCIENCE**

John Clarke, Program Leader

**NOVEL OPTICAL TECHNIQUES ALLOW STUDY OF  
POLYMERIZATION OF MOLECULAR MONOLAYERS**

CAM scientists under the direction of Y.R. Shen have recently developed novel nonlinear optical techniques that allow the direct study of the polymerization of molecular monolayers. The first, optical second harmonic generation (SHG), has been shown to be highly sensitive and surface specific, and affords excellent spatial and temporal resolution. Its effectiveness was demonstrated in following the polymerization of monolayers of octadecyl methacrylate, and also of vinyl stearate monolayers spread on water. The other technique, third harmonic generation (THG) is less surface specific, but is applicable to polymers that are symmetric, and therefore invisible to SHG, but have large third-order nonlinearity. It has allowed observation of the very interesting phase transition of a monolayer of the polydiacetylene, 4 poly-BCMU, on water from the "yellow" form to the "red" form under surface compression.

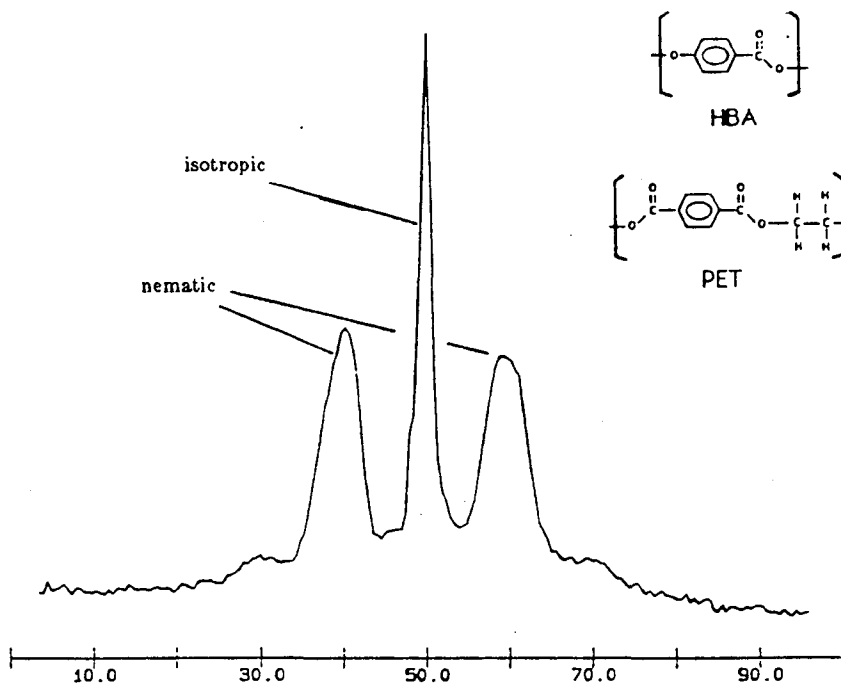
The ability to study the reactivity and kinetics of polymerization under variable and controllable conditions of molecular separation and orientation make SHG and THG powerful techniques in the study of polymerization events. Application of these techniques to materials of industrial interest are being pursued, for example in a collaborative project with M. W. Kim, Exxon Research & Engineering Company who is at CAM for three months as part of the Industry-Laboratory Technology Exchange Program.

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G. Berkovic, T. Rasing, and R. Shen, Study of monolayer polymerization using nonlinear optics, *J. Chem. Physics*, vol. 85, 1986.

G. Berkovic, R. Shen, P.N. Prasad, Third harmonic generation from a monolayer film of a polydiacetylene poly-4-DCMU, *J. of Chem. Phys.*, in press.



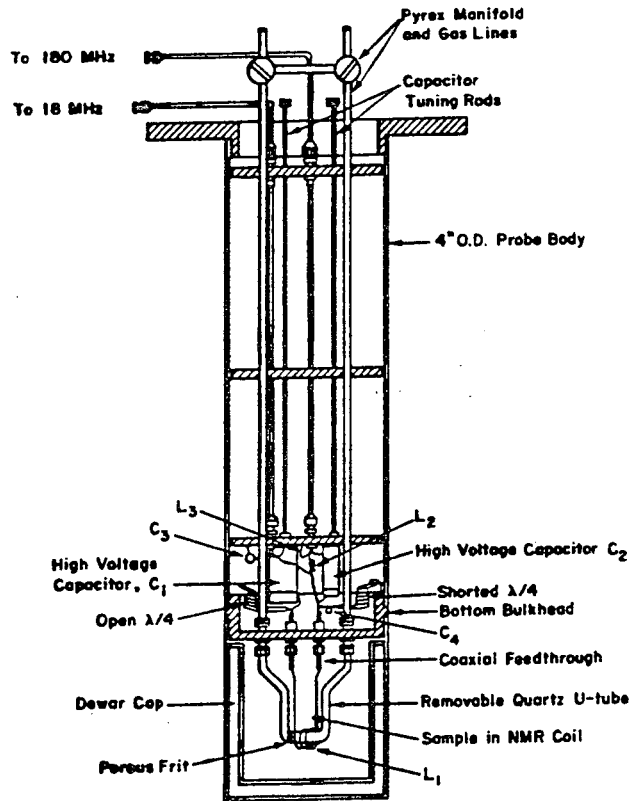


Liquid state NMR spectrum of a copolyester containing 60% p-hydroxybenzoic acid (HBA) and 40% poly(ethylene terephthalate) (PET)

**POLYMERS AND COMPOSITES****Morton M. Denn, Program Leader****VISCOSITY ANOMALIES IN LIQUID CRYSTALLINE  
POLYMERS EXPLAINED AT MOLECULAR LEVEL**

Liquid crystalline polymers that can be processed in the molten state hold great promise for high-performance applications because of their exceptional strength, high melting point, and chemical resistance.

As part of a continuing effort to understand the molecular basis for these properties, polymers researchers at CAM have recently used high-temperature liquid NMR spectroscopy and mechanical rheometry (stress-deformation) measurements to resolve previously unexplained anomalies in the viscosity of liquid crystalline polymers that have been subjected to deforming forces. They have found that these anomalies are a consequence of the simultaneous existence of two types of molecular arrangements in the molten material: a liquid crystalline (nematic) fraction in which the individual molecules are aligned parallel to each other, and an unordered (isotropic) fraction. (The isotropic areas cannot be observed with optical microscopy or differential scanning calorimetry and have thus remained undetected until now.) The group has also found that the relative amounts of these two states depend on how the material was processed and on the molecular weight. This suggests that control of the proportion of the two states can be accomplished, and that this control might allow achievement of the superior properties of the polymer required for high performance applications. The study is continuing with the examination of a series of polymers of different monomer ratios being synthesized specifically for CAM by the Eastman Chemical Division of Kodak.



NMR probe for *in situ* studies of catalysts

**SURFACE SCIENCE AND CATALYSIS**

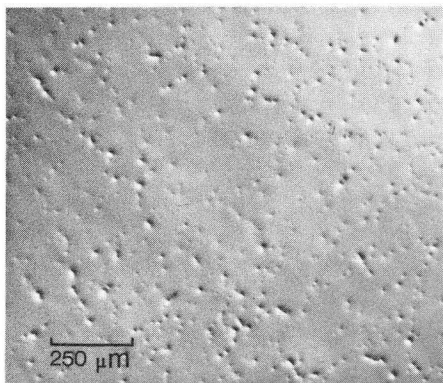
Gabor Somorjai, Program Leader

**NMR PROBE DEVELOPED TO ALLOW REAL-TIME  
OBSERVATION OF CATALYST REACTIONS**

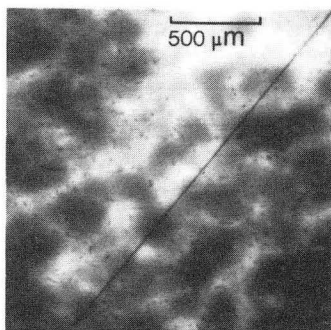
CAM scientists under the direction of J.A. Reimer have developed a unique *in situ* probe that significantly broadens the applicability and value of nuclear magnetic resonance spectroscopy (NMR) to the study of surfaces and catalysts.

NMR has emerged as a powerful molecular probe in the study of the structure and motion of adsorbates, (molecules that have been adsorbed onto catalyst surfaces). Until now, however, investigators have prepared their samples in a sealed tube that can be placed within the coil of the NMR probe and studied only after preparation is complete and all reactions run. The effect of a reaction could be studied only by removing the tube from the coil, performing the new reaction and then returning the tube to the coil for reexamination and comparison to the pre-reaction results.

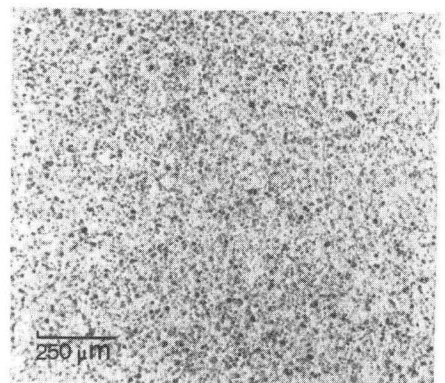
The new CAM probe contains a built-in micro-reactor that allows for the continuous NMR spectroscopy of the changing state of the catalyst and the reacting molecules as a reaction progresses. It functions at temperatures from  $-200^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ , and offers a number of new and exciting experimental opportunities. CAM scientists have used it to study the adsorption of molecules on high surface area catalysts which can be synthesized and activated only in an oxygen-free environment. Systematic studies of adsorbate coverage of catalyst surface have been performed by continuously adjusting the concentration of adsorbed molecules in the reactor without breaking vacuum. The effect of altered temperatures on the reactions has also been studied, for example in reactions of hydrogen and ammonia on high surface area  $\text{MoN}_2$  allowing for the first time, the correlation of the geometric arrangement of catalyst and adsorbate with the energetics of site adsorption. Other uses for the probe, including studies of polymer flows and biological activity at elevated temperatures, are being explored.



a) section of GaAs wafer with  $^{14}\text{C}$  after photoetching



b) scanning photoluminescence image of same area of the wafer



c) autoradiograph of same area

## ELECTRONIC MATERIALS

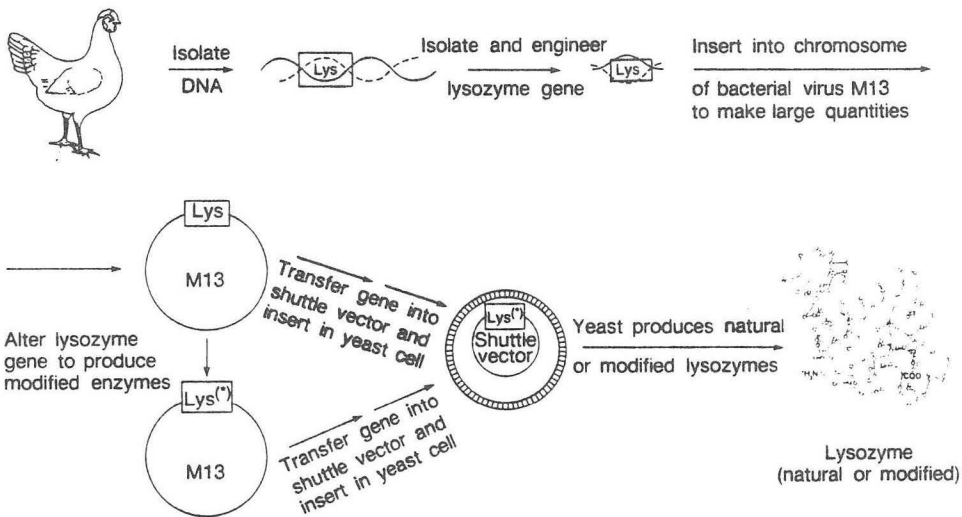
Eugene Haller, Program Leader

### FIRST DIRECT MICROSCALE MAPPING OF CARBON IN GaAs

CAM scientists have achieved the first direct imaging of the distribution of carbon atoms in gallium arsenide (GaAs) crystals.

Photoetching and high resolution scanning photoluminescence images of cross-sectional wafers of GaAs crystals reveal localized defects such as dislocations (misalignment of atoms). The photoluminescence images also reveal inhomogeneities around the dislocations. The cause of inhomogeneities and their effects on the performance of devices such as GaAs field-effect transistors, are still a subject of intense debate in the research community. To achieve a more detailed understanding of the problem, and specifically the role of carbon atoms, CAM scientists E.E. Haller and E.D. Bourret introduced radioactive carbon into GaAs crystals in the form of  $^{14}\text{C}$  enriched barium carbonate added to the melt. X-ray film exposed to the  $\beta$  particles from the decay of  $^{14}\text{C}$  located near the wafer surface revealed the distribution of carbon. Comparison with the photoetching and photoluminescence images of the same wafer demonstrated that the carbon is distributed homogeneously and not, as others have proposed, preferentially at the dislocations.

The ability to conclusively rule out carbon as the cause of the observed inhomogeneities near dislocations represents a major step towards an understanding of the coupling between materials properties and device performance. It also helps lay the basis for possible adjustments in crystal growth conditions to allow production of crystals that are better suited for use in these devices.



Cloning, Expression and Genetic Engineering of Chicken Lysozyme Gene

**ENZYMATIC SYNTHESIS OF MATERIALS****Mark Alper, Program Leader****GENE FOR MATERIALS SYNTHESIS ENZYME  
CLONED AND EXPRESSED IN YEAST**

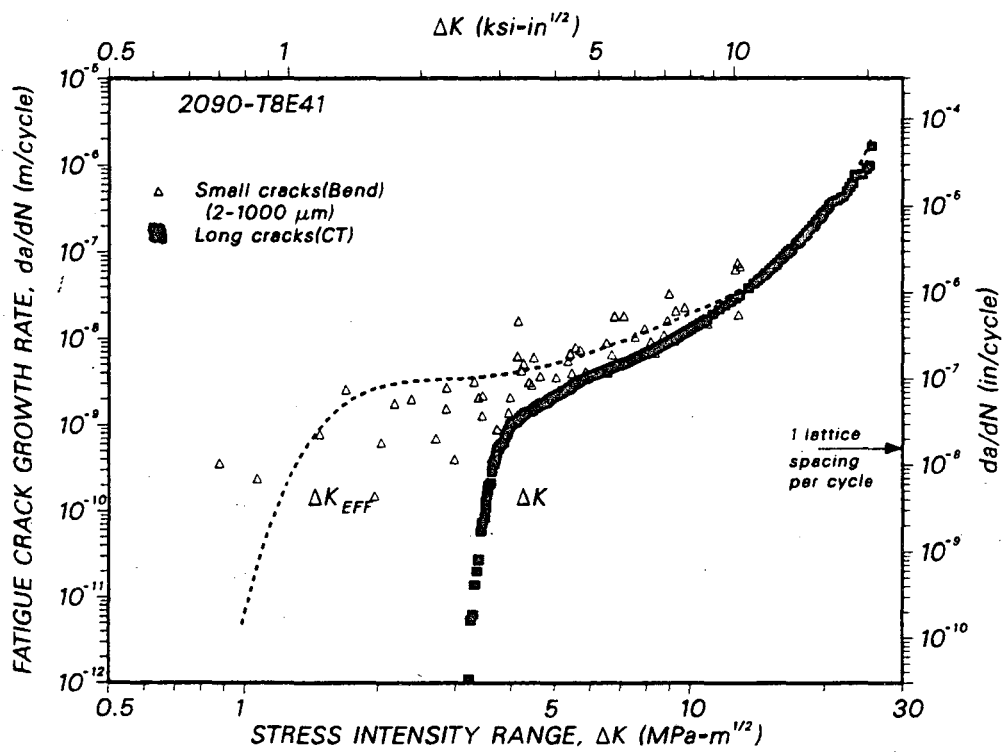
CAM scientists, under the direction of Prof. J.F. Kirsch, have, for the first time, created a laboratory strain of yeast that produces large quantities of the enzyme lysozyme for use in materials synthesis.

This work was done in collaboration with Dr. Steven Rosenberg at Chiron Corporation, a biotechnology company in Emeryville, California. It was achieved by transferring (cloning) the lysozyme gene from chickens, where the enzyme is produced to protect the egg from bacterial infection. In the course of this genetic manipulation, the gene was also modified so that it would be transcribed to make RNA and therefore protein at very high efficiency, and so that the lysozyme produced would be secreted through the yeast cell membrane into the growth medium.

The lysozyme produced by the yeast has been shown to fold properly into its three-dimensional structure and is catalytically active. As much as 30% of the total protein in the medium is lysozyme; thus its isolation and purification is significantly simplified. Routine industrial scale-up should allow production of tens of grams per run.

Specific variants of the lysozyme gene, are now being genetically engineered by program molecular biologists to produce mutant enzymes with altered substrate binding properties. Large amounts of these enzymes will also be produced by cloning. Their genes will be introduced into this same yeast strain using the identical procedures developed for the "wild-type". The new enzymes will be used to attempt synthesis of novel polymers never before made either in nature or in the laboratory.





XBL 871-357

Comparison of the growth rates of long ( $\geq 5$ mm) and microstructurally-small (2 to 1000  $\mu$ m) fatigue cracks in 2090-T8E41 alloy.

**STRUCTURAL MATERIALS****J.W. Morris, Jr., Program Leader****Al-Li ALLOYS SHOW UNEXPECTED  
CRACK GROWTH RATES**

Alloys of aluminum and lithium have recently been targeted for many potential aerospace applications due primarily to their low density (and therefore light weight), high toughness at extremely low temperature, and superior resistance to the growth of fatigue cracks.

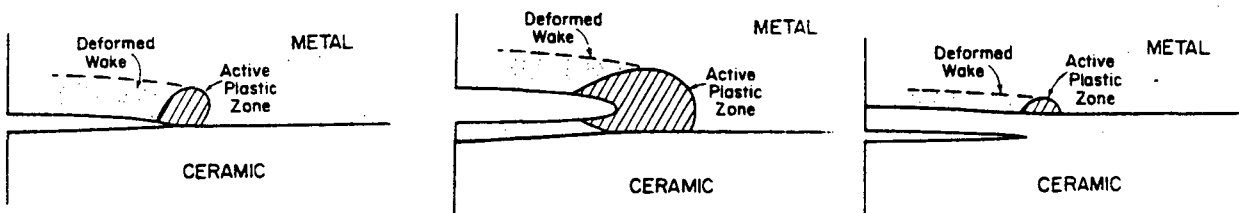
Conventionally, the fatigue resistance has been assessed by monitoring the rate of the growth of "long" cracks, typically those in excess of 10 mm in length. However, the lifetime of actual in-service components is often dominated by the growth of far smaller cracks. Recent studies at CAM under the direction of R. O. Ritchie have shown that while prominent aluminum-lithium alloys, such as 2090-T8E41, have better "long" fatigue crack growth properties than traditional high strength aluminum alloys, their "small crack" properties may be worse. The discrepancy between the behavior of the "long" and "microstructurally-small" cracks has been explained in terms of the microstructural mechanisms of crack advance, specifically involving Ritchie's concept of crack tip shielding.

These results suggest that the use of aluminum-lithium alloys such as 2090-T8E41 may well improve the fatigue life of components employed in many future aerospace applications, although this superior fatigue crack growth resistance may not be fully realized in those components whose life expectancy is dominated by crack initiation or the early growth of small flaws.

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K.T. Venkateswara Rao, W. Yu, and R.O. Ritchie. *Scripta Met.*, vol. 20, Oct. 1986, pp. 1459-65.

K.T. Venkateswara Rao, W. Yu, and R.O. Ritchie. *Metall. Trans. A.*, vol. 18A, in press.



The crack location and amount of plastic work accompanying propagation determine the fracture energy.

**CERAMIC AND METAL INTERFACES**

Rowland Cannon, Program Leader

**DELAMINATION OF CERAMIC-METAL  
INTERFACES REDUCED THROUGH ENERGY  
ABSORPTION BY METAL LAYER**

Electronic devices in which thin layers of metal are in contact with layers of ceramic are becoming increasingly important in the manufacture of semiconductor chips and their supports. Development of these devices has been impeded however because the interfaces between the metal and the ceramic are sensitive to delamination resulting from strains that arise in the device during either the manufacturing process or the repeated heating and cooling cycles that occur during use.

Scientists at CAM have been exploring alternative designs for these devices in which the strain energy would be directed away from the interface and thus its delamination or cracking would be reduced. They have recently demonstrated the feasibility of this approach: analysis using electron microscopy has revealed the presence of a high density of atomic dislocations in the copper layer of a copper/ceramic interface. These harmless dislocations can be attributed to the diversion into the copper of a large fraction of the strain energy that would otherwise have caused delamination. This conclusion is supported by experiments that showed that under conditions that limit energy absorption by the copper, far less force is required to crack the interface. These results are being used to aid program scientists both to develop a detailed understanding of the relationships between interfacial bonding and fracture energy, and also to use that understanding in the design of advanced devices.

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