DISCLAIMER

Materials and Molecular Research Division

Newsletter

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RESEARCH PROFILE

Mitchel Shen

PROPERTIES AND MORPHOLOGY OF POLYMERIC ALLOYS

During the past few decades, synthetic chemists have made literally thousands of new polymers with various novel properties. However, it has been estimated that only 1 or 2% of these materials ever find widespread use. In fact, out of the nearly 30 billion lbs. of synthetic rubbers and plastics produced in the U.S., about 80% is taken up by a few well-known polymers such as polyethylene, polystyrene, polybutadiene, etc. Clearly the most efficient way to find polymeric materials for large-scale applications is to combine the existing polymers in such a manner that the resulting new materials have the desired properties. It is this need, plus the potential of generating new materials of unusual properties, that has stimulated the level of research in polymeric alloys.

Polymeric alloys are multicomponent polymers in which the components exist on a polymeric level. They include block copolymers, graft copolymers and polyblends. Because of their long chain nature, polymer molecules in the amorphous state generally already possess high entropies. Thus the gain in entropy due to mixing two or more dissimilar

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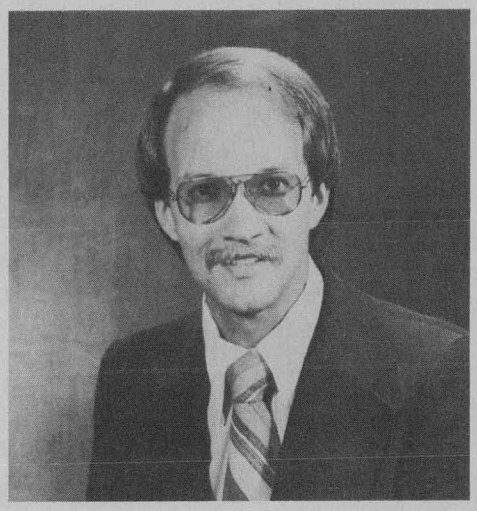

GRONSKY WINS GOLD (HARDY MEDAL)

DR. RON GRONSKY, investigator with our Division and lecturer in the MS & ME Department on the Berkeley Campus, was the 1979 recipient of the Robert L. Hardy Gold Medal of the Metallurgical Society of the American Institute of Mining, Metallurgical & Petroleum Engineers. DR. GRONSKY received the award at the AIME Annual Meeting in New Orleans, February 20, 1979.

The Hardy Gold Medal is given annually to the most outstanding young metallurgist in the U.S.A. under the age of 30. DR. GRONSKY, a member of Professor GARETH THOMAS' electron microscopy group, is noted for his work in the utilization of high resolution microscopy for the study of grain boundary structure and precipitation; and for fundamental studies of spinodal phase transformations in alloys.

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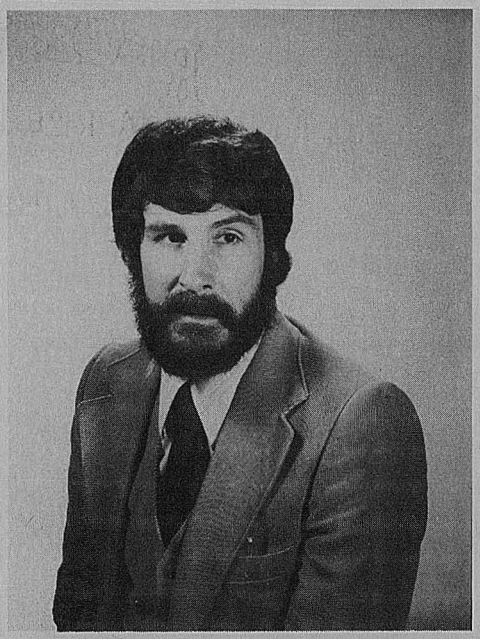

MCARTHUR JOINS STAFF AT MMRD

He's a Leo.
He's a Pennsylvanian.
And he went to Cornell.

KENT MCARTHUR joined the MMRD administrative staff at the beginning of 1979 as CONWAY PETERSON's assistant. He will be training on all aspects of the position with special attention to budgeting, data processing and special projects.

KENT brings some impressive credentials to his new post. KENT obtained most of his education in the East, finishing the formal years at Cornell University where he received his Master's in Management Science. What, you wonder, is Management Science? KENT explains, "It's intensive training in operations research, industrial engineering, and in examination of the quantitative aspects of management."

After Cornell, KENT worked for ESSO (now Exxon), including a stint in London, England, prior to heading out West to California. He worked several years for FMC Corp. in an operations planning and analysis group. When FMC Corp. transferred their corporate headquarters to Chicago, KENT joined Guild Wineries and Distillers, makers of Cresta Blanca Wines, where he was associated with the Logistics and Planning functions.

This job with MMRD intrigues KENT greatly: "I've never worked in a non-profit oriented environment before. I believe the academic, research and government milieu will be quite challenging and open new career vistas.

KENT is a good listener--so good, in fact, that an interviewer must be careful to allow him to talk. Perhaps his pronounced interest in the behavioral sciences--a field in which he reads extensively--explains his listening skill.

In addition to reading, he also enjoys racketball, handball and chess. He is married and father of two youngsters, QUINN, 12; and MAGGIE, 10. Mrs. MCARTHUR, KATHLEEN, is very active in volunteer work at the children's schools.

Since joining MMRD, he has spent much of his time meeting people and becoming acquainted with administrative procedures in the Division. However, he can often be found during lunch playing spades with LEARR, CATHY, CAROL, and DEBBIE. He likes those odds!

Thursday evenings, KENT teaches a seminar on management at Armstrong College in Berkeley. A big smile breaks over his bearded face, "I enjoy teaching. It gives me a chance to preach what I practice!"

◆

QUOTE

"To punish me for my contempt for authority," Einstein wrote, "fate made me an authority myself."

GRONSKY (continued)

RON's current major responsibility with MMRD is to develop the atomic resolution electron microscopy program.

Receipt of this high honor crowns other recent achievements by RON: he won the John E. Dorn Memorial Award for 1978, as well as taking second place for use of unique or unusual techniques in microscopy at the 1978 International Metallographic Society Exhibit.

RON was born in Pittsburgh, PA. in 1950, but now lives with his wife and two children in El Cerrito, California.

RESEARCH PROFILE (continued)

polymers is small, and as a consequence most polymers do not mix. However, special precautions are exercised in the synthesis of polymeric alloys, so that phase separations in these systems remain at a microscopic level. For example, in the case of block copolymers, the dissimilar chains are connected to each other via covalent bonds. Because of these special constraints polymeric alloys often exhibit rather unique morphological features, the study of which (by electron microscopy, small angle x-ray scattering, neutron scattering, etc.) has contributed significantly to our understanding of the structure of these materials.

Because organic polymers all contain carbon atoms, the application of electron transmission microscopy requires the selective introduction of heavy atoms for observation. These staining agents, such as osmium tetraoxide or bromine, are believed to react with double bonds. Because of the greater cross section to the electron beam provided by these heavy atoms, the necessary contrast is obtained in polymeric alloys in which one of the components contains double bonds. For example, Fig. 1 shows the electron micrograph of a block copolymer consisting of polystyrene and polybutadiene blocks (SBS). The dark regions represent the polybutadiene domains which have been stained by OsO_4.

An interesting phenomenon of strain-induced plastic-to-rubber transition has been observed in appropriately prepared SBS samples. It is well known that plastic materials have relatively high initial modulus (10^3-10^4 MPa), but fracture at a relative low strain (<5%). They can also be made to undergo yielding to result in irreversible deformation. On the other hand, elastomeric materials exhibit high elasticity though with low modulus (1-10 MPa). In the case of SBS, it is possible to prepare a plastic-like specimen with the rigidity

(Continued page 4)

Fig. 1. Transmission electron micrograph of a block copolymer consisting of polystyrene and polybutadiene blocks (SBS).

RESEARCH PROFILE (continued)

modulus usually associated with plastic materials. When it is stretched beyond its elastic limit, it will also undergo apparent yielding. However, the necked region does not suffer irreversible deformation. Rather the plastic-like material has been transformed into rubber-like material. At the conclusion of the transformation process, the entire sample behaves like an elastomer and can be stretched reversibly for thousands of times up to 600% strain or higher without fracture. If now the sample is allowed to recover without the application of external stress, it will revert back to the original plastic condition in a few days. The recovery process can be accelerated by heating. For instance, at 60°C the rubber is transformed back to plastic in a few minutes.

Figure 2 shows the small angle x-ray scattering data of SBS. The scattering profile for the unstretched sample is fairly sharp, indicating a reasonably regular morphology. Upon stretching, the profile becomes more diffused and the peak position is shifted to a higher angle. The implication here is that the structure now becomes more irregular,

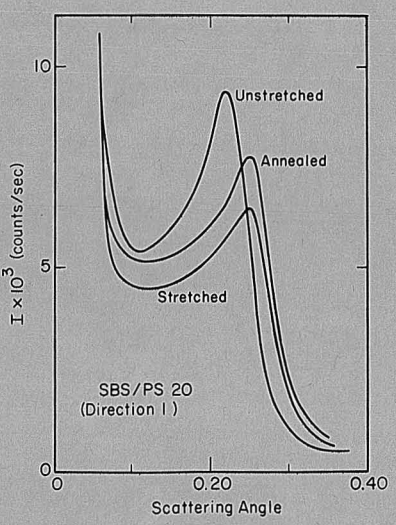

Fig. 2. Small angle scattering data of SBS.

and the interdomain distances have decreased. However, annealing appears to shift the curve back toward the original unstretched state. The most plausible interpretation of these data is that stretching the sample destroys the connectivity between the polystyrene domains, resulting in irregular fractured fragments. Thus the sample now behaves like an elastomer. Annealing has brought the morphology back to the original state, thus the sample becomes plastic-like again.

A more direct demonstration of these changes is shown in Fig. 3. This figure shows the transmission electron micrograph of an SBS sample in the stretched state. Note the appearance of chevron-like structures as well as the fragmented polystyrene (white) domains, which were not present in the original unstretched sample (Fig. 1).

On the basis of these data, we can now propose a qualitative mechanism of the observed strain-induced plastic-to-rubber transition of block copolymers. In Fig. 4 we show the idealized schematic diagrams of this transformation process. The original lamellar structure of the unstretched sample in (A) upon stretching first deforms by

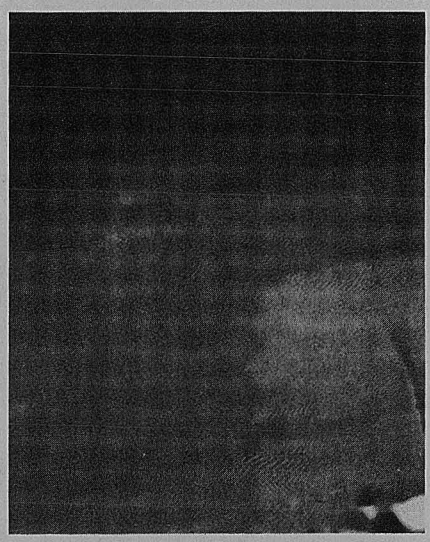

Fig. 3. Transmission electron micrograph of SBS in the stretched state.

RESEARCH PROFILE (continued)

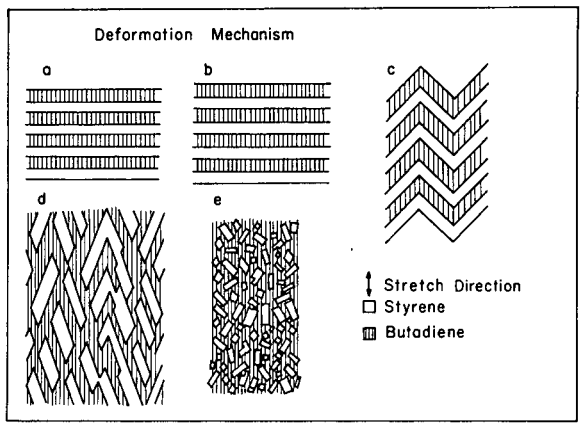

Fig. 4. Schematic diagram of the mechanism of strain induced plastic-to-rubber transition of SBS block copolymer.

enlarging the interdomain distances (B). When the elastic limit is exceeded, the deformation continues by distorting the lamellae into chevron-like structures (C). As the strain increases further, the domains are fractured in the manner given by (D) and (E). Thus the plastic-like properties of the block copolymer is due to the connectivity among the plastic domains, while the rubber-like properties result from the dispersion of the fractured plastic domains in the elastomeric matrix. Annealing reverses the process by going from (E) back to (A), and the original plastic-like sample is recovered.

The above example illustrates one aspect of the behavior that can be produced in polymeric alloys. By a judicious choice of proper components and techniques, polymeric materials with unique properties can be synthesized. We are at a point where the property-structure correlations for polymeric alloys are just beginning to be explored. It is to be hoped that more efforts in this regard will not only elucidate the basic mechanisms, but also open new potentials for future applications of these materials.

CONFERENCE ON CORROSION/EROSION IN COAL CONVERSION MATERIALS

On January 24-26, a Conference on Corrosion/Erosion of Coal Conversion Systems Materials was held at the Berkeley Marina Marriott Inn. One hundred fifteen registrants representing industry, government laboratories and universities both here and abroad, plus some 35 students and professors from UCB attended the meetings.

The Conference was divided into three sessions: combined corrosion/erosion behavior; corrosion behavior; and erosion behavior, and featured 15 invited papers. An additional 10 papers selected from a large group of submitted abstracts made up an in-progress research session. The final facet of the meeting used a workshop format where four separate groups met in the evening to formulate recommendations for future research directions. Each group's moderator presented the results of these discussions the next day.

Dr. Stanley Wolf and Dr. Walt Bakker from the Washington Headquarters of DOE attended the Conference. Dr. Wolf presided over the final session dealing with future research directions.

Since the Conference was held here in Berkeley, the bulk of the coordinating fell on AL LEVY and CAROL PAYNE. Credit for the success and smooth unfolding of the conference goes to them.

The Conference, jointly sponsored by MMRD, the National Association of Corrosion Engineers (NACE), and the Materials Sciences Division of DOE, was well received by the attendees. Proceedings of the meetings will be published by NACE.

FIRE IN BUILDING 62

Four-thirty, Thursday morning, February 8, 1979.

All is quiet.

One minute later the heat alarm in Rm. 248, Building 62 sounded.

By 4:55 AM firemen and equipment began arriving at the fire site where they quickly put out the fire and began a clean-up and evaluation of the damage.

It seems virtually certain that an oil leak from the vacuum pump bearing seal was the physical cause of the fire. The pump dripped oil onto the rotor belt. Gradually the belt became impregnated. It began to slip, placing increasing demands on the electric motor which in turn grew hotter. Each weakness compounded the friction on the next component. The motor bearings began warming beyond normal; the mount grew warm.

DRUCILLA DAVIS, graduate student experimenter, had carefully arranged an electric hair dryer set to cold to cool the molecular sieve trap attached by a rubber hose to the mechanical pump which ran continuously. The rubber mount was not cooled--there was not expectation of heat concentration there.

The overheated bearings spun. The mount began to smolder; suddenly it flared. Igniting the thin plywood on the desk located above the experiment, the fire destroyed the desk and began spreading up the west wall of the laboratory. Heat in the room rose rapidly, triggering the heat alarm and bringing the firemen.

The sweep of the fire up the west wall of the laboratory produced

CHIEF SILVA EXAMINES FIRE SITE

an unexpected effect: the soft copper solder used on the valves of the water lines near the ceiling melted when the temperature exceeded 414°F allowing water to spray across the lab. Water damage increased the loss from the fire although it did aid in controlling the flames.

Estimated loss from the fire is $9648.00.

Chief Silva, after careful examination of the damaged area, made four recommendations (paraphrased below):

1. Remove wooden desks from experiment areas.
2. Do not allow mechanical pumps beneath combustible furniture.
3. Remove all high water piping except those specifically required at that height.
4. Minimize combustible storage in laboratories.

QUOTE

"Automatic recall should be visited on anyone on the public payroll who says 'viable.'"---Edwin Newman in "Strictly Speaking"

189's

Directions for preparation of the 1979 form 189's--now retitled, "Field Task Proposal/Agreement," are out to all investigators and secretaries in the Division.

Deadline for return of requested material is 2/28/79! Watch that deadline!

ANNUAL REVIEWS END

After some hectic behind-the-scenes heroics, the MMRD Annual Review passed into history. Many of our visitors remarked on the smoothness of the Reviews--only we who labor behind the front know the agony and the ecstasy these gatherings produce!

PEOPLE NEWS

Dr. NORMAN EDELSTEIN recently contributed a chapter entitled "Electronic Structure of f-Block Compounds" to a book Organometallics of the f-Elements, edited by T. M. Marks and R. D. Fischer, to be published shortly by Riedel and Co.

♦

Professor ANTHONY EVANS presented an invited paper at a joint meeting of the American Society of Acoustics and the Japanese Acoustics Society in Honolulu, Hawaii. ANTHONY'S paper was entitled "Acoustic Emission Sources in Brittle Solids."

♦

CARL LAMPERT and JACK WASHBURN are co-authors of a paper presented by CARL at the SERI-DOE Solar Collector Coatings Conference in Boulder, Colorado, in late January. Title of the paper: "Microstructure and Optical Properties of Black Chrome Before and After Exposure to High Temperatures."

♦

MARY NORTON, secretary for Professors CLARKE and RICHARDS, has moved her office. She is now in Bldg. 19A, Rm 347. Her phone number moved with her.

CORDELLE YODER has set the date! She will show the slides from her recent trip through New England and into Canada between 12:00 and 1:00 PM on Monday, February 26 in Room 306 Latimer Hall on Campus. CORDELLE timed her trip to take in the magnificent fall leafage in the East. Brown-bag it Monday. See you there!

♦

JOAN AMOROSO, secretary for Dr. JEFFRIES Group, has a bird feeder on a ledge just outside the window of her campus office. Among her frequent visitors to the ledge are towhees, wrens, doves, jays, and an occasional cowbird.

♦

PHILA WITHERALL ROGERS, formerly a photographer with IMRD before our name change to MMRD, and currently a writer on the LBL Newsmagazine, has two stories and a number of photographs in the January-February issue of the California Monthly. For those of us who work on the hill, the article on Strawberry Canyon is particularly interesting. Write on, PHILA.

PEOPLE NEWS (continued)

Professor MARVIN COHEN is on the Program Committee for the 3rd Conference on Superconductivity in d- and f-Band Metals to be held at UC San Diego, La Jolla between June 21-23, 1979. MARVIN is on a Guggenheim in Hawaii, but he still keeps a hand in the action!

♦

Have you ever seen a gloxinia in bloom?

With a velvet-textured deep bell-shaped bloom, they are one of the most spectacular houseplants you can pamper. WINNIE HEPPLER, scientist in Dr. SHIRLEY'S research group, has a couple of royal purple blooms adorning the gloxinias in her work area. They're beautiful, WINNIE.

♦

Dr. ROBERT RITCHIE, former scientist with MMRD, now located at MIT, dropped by on January 31 for a visit with old friends at the Laboratory. ROB was attending a meeting in San Francisco and seized the opportunity provided by the trip to drop in briefly.

♦

If Professor JOHN WINN looks perplexed these days, he is! Seems he received a large manila envelope from AAAS with a dramatic caption outside saying important new benefits for AAAS members inside. But . . . . the envelope arrived empty!

♦

Professor GLENN T. SEABORG, Associate Director at Large of the Lab, is the editor of Transuranium Elements: Products of Modern Alchemy. This is Volume 1 of the Benchmark Series in Physical Chemistry and Chemical Physics. Publisher is Dowden, Hutchinson & Ross, Inc.

LBL REPORTS BY MMRD PERSONNEL

NOTE: All MMRD/LBL reports listed here are available in the reference section of the MMRD Library, Bldg. 62, Rm. 339, or call Marianne Larsen, Librarian, at Ext. 5971 (p.m. only)

LBL-6293: Models for Kinetics of Solid State Sintering ... *B. Wong and J. A. Pask.*

LBL-6294: Experimental Analysis of Sintering of MgO Compacts ... *B. Wong and J. A. Pask.*

LBL-7687: Reactive and Nonreactive Scattering of Modulated Molecular Beams from Well Characterized Platinum Single Crystal Surfaces ... *R. J. Gale* ... (Ph.D. thesis).

LBL-8203: Potential Distribution for Disk Electrodes in Axisymmetric Cylindrical Cells ... *P. Pierini and J. Newman.*

LBL-8208: Vibrational Energy Transfer In Selectively Excited Diatomic Molecules ... *C. J. Dasch* ... (Ph.D. thesis).

LBL-8215: Electron Microscopy Study of Microsegregation and Defects in Czochralski Grown Calcium Gallium Germanium Garnet Single Crystals ... *T. F. Roth* ... (M. S. thesis).

LBL-8282: A Classical Analog for Electronic Degrees of Freedom In Non-Adiabatic Collision Processes ... *H.-D. Meyer and W. H. Miller.*

LBL-8294: Bonding in Inorganic Compounds: A Study by X-ray Photoelectron Spectroscopy ... *S. C. Avanzino* ... (Ph.D. thesis).

LBL-8317: Transient Behaviour of Porous Electrodes with High Exchange Current Densities ... *R. Pollard and J. Newman.*

LBL-8368 Abs.: Dynamics of the Photodissociation of Ozone ... *L. R. Carlson, R. K. Sparks, K. Shobatake, M. Kowalczyk, H. S. Johnston, and Y. T. Lee.*

LBL-8376: Direct Observation of the Growth of Voids in Multifilamentary Superconducting Materials via Hot Stage Scanning Electron Microscopy ... *J. L. Wang, J. T. Holthuis, M. R. Pickus, and R. W. Lindberg.*

LBL-8406: Crossed Molecular Beam Studies on the Interaction Potentials for $F(^2P)$ + Ne,Ar,Kr(^1S) ... *C. H. Becker, P. Casavecchia, and Y. T. Lee.*

LBL-8421: Anomalous Scattering By Cobalt and Chlorine and Crystal Structure of(+)-Tris (Ethylenediamine)Cobalt(III) Chloride (+)-Tartrate Pentahydrate ... *D. H. Templeton, A. Zalkin, H. W. Ruben and L. K. Templeton.*

LBL-8425: Classical Model for Electronic Degrees of Freedom in Non-Adiabatic Collision Processes: Pseudo-Potential Analysis and Calculations for $F(^2P_{1/2}) + H^+, Xe \rightarrow F(^2P_{3/2}) + H^+, Xe$ ... *C. W. McCurdy, H. D. Meyer and W. H. Miller.*

LBL-8440: Fundamentals of the Particulate Phase in a Gas-Solid Mixture ... *W.-S. Yeung.*

LBL-8443: Infrared Measurements of Molecules Adsorbed on Metal Surfaces, A Low Temperature Thermal Detection Technique ... *R. B. Bailey and P. L. Richards.*

LBL-8444: Infrared Measurements of Electrons Trapped on the Surface of Superfluid Helium ... *D. K. Lambert and P. L. Richards.*

LBL-8445: Far Infrared Sky Survey ... *S. E. McBride, P. L. Richards, and D. P. Woody.*

LBL-8457: The Electronic Structure of UCl_6: Photoelectron Spectra and Scattered Wave Xα Calculations ... *G. Thornton, N. Edelstein, N. Rösch, R. G. Egdell and D. R. Woodwark.*

LBL-8465: Chloro-, Methyl-, and Tetrahydroborato- Tris (Hexamethyldisilylamido)-Thorium(IV) and Uranium(IV). Crystal Structure of Tetrahydroborato Tris (Hexamethyldisilylamido) -Thorium(IV). . . *H. W. Turner, R. A. Andersen, A. Zalkin, and D. H. Templeton.*

LBL-8466 Abs.: Dynamics of Multiphoton Dissociation in Molecular Beams ... *Aa. S. Sudbø, D. J. Krajnovich, P. A. Schulz, Y. R. Shen, and Y. T. Lee.*

LBL-8473: Structure Sensitivity in Electrocatalytic Properties of Pt: II. Oxygen Reduction on Low Index Single Crystals and the Role of Steps ... *P. N. Ross, Jr.*

LBL-8475: Zero Pressure Lifetimes and Fluorescence Quenching of $ICl(A^3\Pi_1)$ ... *S. J. Harris, W. C. Natzle, and C. B. Moore.*

LBL-8478: Semiclassical Statistical Mechanics of Fluids: Nonperturbative Incorporation of Quantum Effects in Classical Many Body Models ... *R. M. Stratt.*

LBL-8505: Electrochemical Reduction of Potassium from Potassium Chloride in Propylene Carbonate Electrolyte with Aluminum Anodes ... *R. Atanasoski, H. Law and C. W. Tobias.*

LBL-8546: Optical Spectroscopy of Aromatic Hydrocarbons on the Ni (111) Surface ... *C. B. Harris, D. A. Zwemer, A. R. Gallo, and H. J. Robota.*

LBL-8548: Chemical Reduction of Refractory Oxides by Atomic Hydrogen ... *D. Dooley, M. Balooch and D. R. Olander.*

LBL-8574: Crossed Molecular Beam Studies on the Interaction Potentials for $Cl(^2P) + Xe(^1S)$ ... *C. H. Becker, J. J. Valentini, P. Casavecchia, S. J. Sibener and Y. T. Lee.*

LBL-8575: Infrared Laser Enhancement of Chemical Reactions Via Collision Induced Absorption ... *A. E. Orel and W. H. Miller.*

LBL-8590 Abs.: Calculation of Properties of the Electron-Hole Liquid in Uniaxially Stressed Ge and Si ... *S. M. Kelso.*

LBL-8591 Abs.: Density Dependence of the Lifetime of the Strain-Confined Electron-Hole Liquid in Ge ... *S. M. Kelso and E. J. Pakulis.*

LBL-8597 Abs.: The Metal-Insulator Transition in Stressed Germanium ... *J. Furneaux and I. Balslev.*

LBL-8600: Reactions and Spreading in the Cu-Ag System ... *P. R. Sharps* ... (M.S. thesis).

LBL-8608: Abrasive Wear in Ceramics: An Assessment ... *A. G. Evans.*

LBL-8610: Stable, Inexpensive, Low Frequency Sine Wave Generator Using Digital Techniques ... *J. Podolske.*

LBL-8611: Stable Sinusoidal Driver Circuit for Tuning Fork Choppers ... *J. Podolske.*

LBL-8633: Thunderstorms as Possible Micrometeorological Sink for Stratospheric Water ... *H. S. Johnston and S. Solomon.*

CALENDAR

SURFACE SCIENCE AND CATALYSIS SEMINARS, 1:00 p.m., Bldg. 62, Rm. 203

Feb. 28: "Oxygen Activated Adsorption on Silver Single Cyrstals," Dr. R. Maddix, Stanford Univ.

March 7: "Catalysis by Metals," Dr. John Sinfelt, Exxon Res. & Eng.

March 14: "Photoelectron Diffraction Effects from Na, Se and Te Atoms Adsorbed on Ni," Dr. Nevil Smith, Bell Telephone Labs.

March 26: "Determination of the Si(III) Surface Reconstruction via Dyramical LEED," Dr. R. Feder Univ. of Jülich, Jülich, W. Germany.

MMRD NEWSLETTER ..... **February 1979**
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