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ANNUAL TECHNICAL REPORT

1989-1990

SUBMITTED TO THE

NATIONAL SCIENCE FOUNDATION

DIVISION OF MATERIALS RESEARCH



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MATERIALS RESEARCH LABORATORY

DIVISION OF THE PHYSICAL SCIENCES

UNIVERSITY OF CHICAGO

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February, 1990

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NATIONAL SCIENCE FOUNDATION
PROJECT SUMMARY

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DIRECTORATE/DIVISION	PROGRAM OR SECTION	PROPOSAL NO.	F.Y.
NAME OF INSTITUTION (INCLUDE BRANCH/CAMPUS AND SCHOOL OR DIVISION)			
The University of Chicago		The James Franck Institute	
ADDRESS (INCLUDE DEPARTMENT)			
5801 South Ellis Avenue Chicago, Illinois 60637		5640 South Ellis Avenue Chicago, Illinois 60637	
PRINCIPAL INVESTIGATOR(S)			
Sidney R. Nagel			
TITLE OF PROJECT			
PROGRAMS IN MATERIALS RESEARCH			
TECHNICAL ABSTRACT (LIMIT TO 22 PICA OR 18 ELITE TYPEWRITTEN LINES)			
Materials research in the Chicago MRL involves close collaborations between theorists and experimentalists from different disciplines and emphasizes the following areas: <u>THRUST I: SURFACE DYNAMICS</u> (Coordinator: S. J. Sibener) A) Adparticle Dynamics and Surface Reactivity, B) Surface Phonon Spectroscopy and Gas-Surface Interactions, C) Seed Area: Structure and Dynamics of Complex Molecular Films, <u>THRUST II: DISORDERED MATERIALS</u> (Coordinators: J. F. Burdett and T. F. Rosenbaum) A) Lower Dimensional Disorder: Mesoscopic and Layered Materials. B) Glassiness and Glassy Dynamics C) Order-Disorder and Structure, <u>THRUST III: DYNAMICAL PATTERNS AND SOLIDIFICATION</u> (Coordinators: L. P. Kadanoff and G. F. Mazenko) A) Dynamical Patterns B) Dynamics of Solidification C) Seed Area: Convective Turbulence . <u>HIGH RESOLUTION ANALYTICAL ION MICROSCOPY AND FOCUSED ION BEAM MICROLITHOGRAPHY</u> (Coordinator: R. Levi-Setti)			

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INTRODUCTION

Management

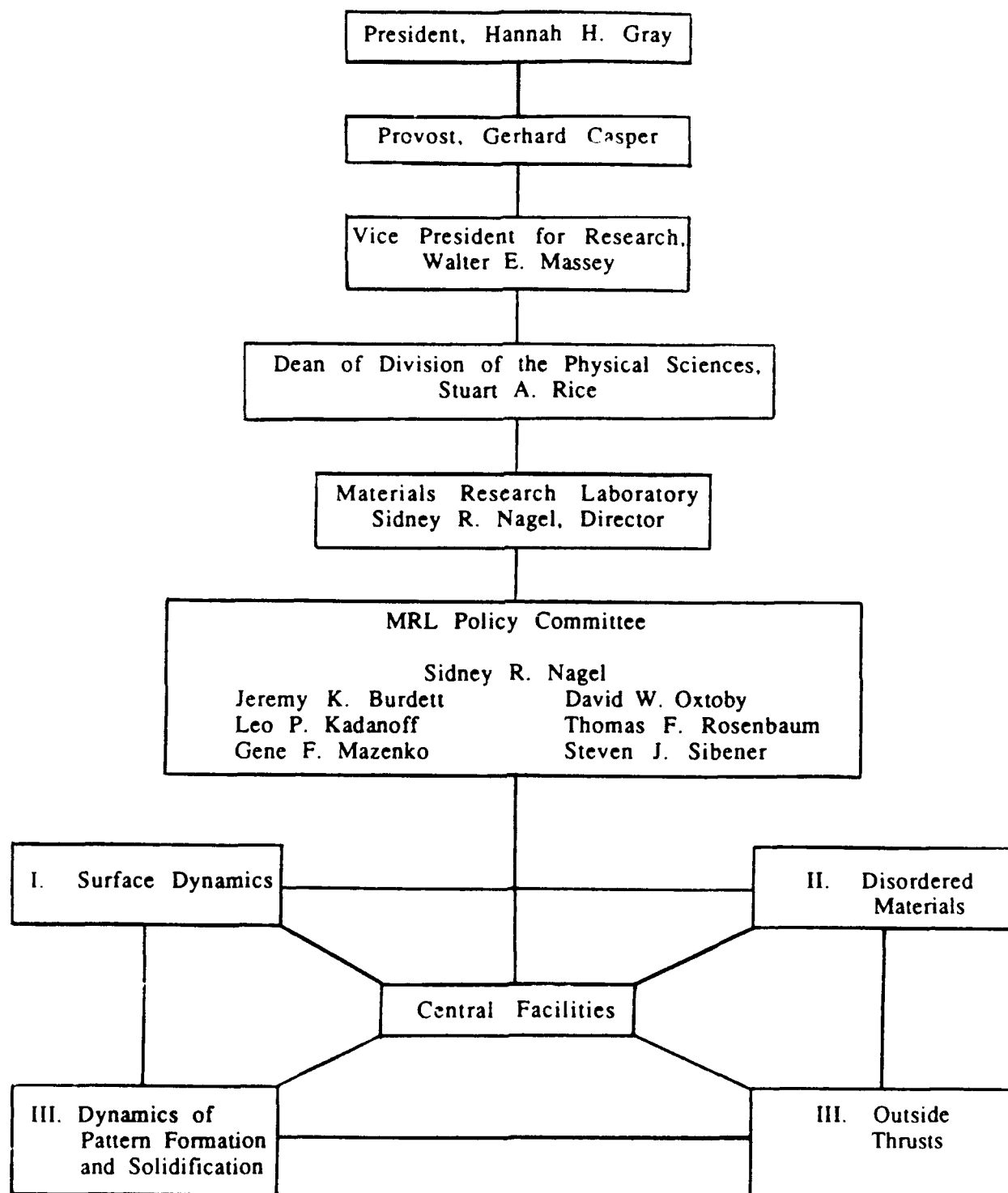
The Materials Research Laboratory at the University of Chicago consists of 22 faculty members who have affiliations with various Departments and Institutes throughout the Physical Sciences Division of the University. The Chemistry, Geophysical Sciences and Physics Departments are all represented as are both the Enrico Fermi Institute and the James Franck Institute. The eight MRL Central Facilities are located both in the Research Institute Building and in the Henry Hinds Laboratory for Geophysical Sciences.

The MRL Program is run by a Director with advice given by a Policy Committee. The Policy Committee is chosen so as to consist of members from each of the Thrusts and with an eye to representing all the different Departmental interests. Both experimentalists and theorists are included. In the last year there has been one change in the composition of the Committee. The seven-member Policy Committee presently consists of:

Sidney R. Nagel	Director, MRL Professor of Physics
Jeremy K. Burdett	Master Physical Sciences Collegiate Division Professor of Chemistry
Leo P. Kadanoff	Professor of Physics
Gene F. Mazenko	Director, James Franck Institute Professor of Physics
David W. Oxtoby	Professor of Chemistry
Thomas F. Rosenbaum	Associate Professor of Physics
Steven J. Sibener	Professor of Chemistry

The Director and the Policy Committee actively encourage new membership in the MRL. It is standard practice that when a new faculty member joins the University in an area that overlaps with Materials Research, he or she is encouraged to submit a proposal. As new members or research proposals are funded, the ongoing Thrusts are scrutinized to see if they are still viable and competitive in light of the changing membership. At times it is necessary to eliminate faculty from the MRL program.

The following block diagram shows how the MRL fits into the University of Chicago administrative organization.



THRUST AREA I. SURFACE DYNAMICS

PERSONNEL

Faculty

J.K. Burdett
 U. Fano
 K. Freed
 R. Gomer
 D.H. Levy
 J.C. Light
 G.F. Mazenko
 S.A. Rice
 S.J. Sibener
 T.A. Witten

Research Associates and Visiting Scientists

A. Auerbach*
 L. Brown*
 T. Curtiss
 E. Daniels
 T. Fässler
 Y. Gong

J.S. Ha
 G. Hose*
 Tzer-Zhen Lin*
 F. Novak
 J. Popielawski
 P. Ruggiero

N. Shamir*
 S. Smithline*
 V. Vladimirov*
 C. Willaims
 Yong Bo Zhao*

Students

S.W. Barton*
 T. Beck**
 P. Braier
 J. Chung
 H. Davis**
 J. Elam**
 B. Gans
 K. Gibson

S. King
 P. Knipp**
 D. Koleske**
 Z.W. Lai*
 J.C. Lin
 W. Menezes
 K. Meyers
 J. Mitchell

L. Niu
 D. Padowitz
 B.N. Thomas
 G. Tisdale
 Z.-G. Wang**
 M. Wedlock**
 L. Xu**
 Y.W. Yang

(On this and later pages, * indicates partial support by MRL, ** principal or exclusive support by MRL.)

Surface Dynamics Organization

Coordinator: S.J. Sibener

- I. Adparticle Dynamics and Surface Reactivity
(Freed, Gomer, Levy, and Sibener)
- II. Surface Phonon Spectroscopy and Gas-Surface Interactions
(Burdett, Fano, Freed, Gomer, Light, and Sibener)
- III. Seed Area:
Structure and Dynamics of Complex Molecular Films
(Freed, Levy, Rice, Sibener, and Witten)

INTRODUCTION:

The MRL effort in Surface Dynamics at Chicago involves researchers in the Departments of Chemistry and Physics who are actively engaged in studying the chemical, electronic, and structural properties of well-defined surfaces using a wide variety of experimental and theoretical techniques. Work in this area is greatly assisted by the close collaborative efforts that have been established between the experimental groups of Gomer, Levy, Rice, and Sibener, and the theoretical groups of Burdett, Fano, Freed, Light, Mazenko and Witten. Additional support comes from the microscopy projects of Levi-Setti, and from the theoretical work of Kadanoff. Burdett and Fano are recent additions who have been intentionally added to this thrust in order to address questions relating to adsorbate-adsorbate and adsorbate-substrate interactions: topics which are of central importance to the experimental programs of Gomer and Sibener. Tom Witten has now joined our MRL, adding increased strength in polymer dynamics and in the interfacial behavior of macromolecules. Virtually all of these groups share many interests with those in the disordered materials section of the MRL. This is particularly true now that our surface thrust is starting to examine surfaces that are partially disordered (with characterized domain structure), or are truly amorphous. Levy's new effort in optical desorption brings further expertise in laser spectroscopy to our MRL effort. His initial efforts will be devoted to studying fundamental aspects of non-resonant laser-induced desorption as applied to medium and large sized molecules - work which will nicely complement the continuing efforts of Gomer in electron induced and thermal desorption, and

Sibener's growing program in laser induced resonant desorption. We are hopeful that the combined efforts of these three programs will lead to an improved understanding of energy flow characteristics in the interfacial region, and how desorption events are influenced by these rates. Theoretical efforts by Freed's group on desorption dynamics and energy flow in excited systems play an important unifying role in these endeavors.

The surface dynamics thrust is divided into three mutually supportive areas. These are (i) Adparticle Dynamics and Surface Reactivity (ii) Surface Phonon Spectroscopy and Overlayer Dynamics and (iii) Structure and Dynamics of Complex Molecular Films. The first of these areas aims at developing a unified picture of the important energetic and dynamical features of gas-surface interactions, up to and including surface reactions. In this view molecules must adsorb onto a surface, diffuse and form, when appropriate, ordered structures, react with each other (or the substrate), and finally desorb as volatile reaction products. Work in this area by Freed, Gomer, and Sibener covers this entire cycle. These activities are directly related to the second topical area, which explicitly aims to improve our understanding of the forces present at clean or adsorbate covered surfaces. Here, major new experimental capabilities have been developed in Sibener's group during the past grant period which can probe surface vibrations with either inelastic neutral particle or inelastic electron scattering. These surface phonon measurements are of crucial importance for many of the topics being pursued in the first topical area (sticking, adsorption-desorption, diffusion, energy disposal in chemical reactions, stability of interfaces

(including roughening), etc. ...). Gomer and Sibener intend to exploit these new experimental capabilities in several collaborative projects. These scattering measurements are supported by a wide range of theoretical initiatives. For example, the quantum scattering calculations of Light help in analyzing elastic and, in the near future, inelastic scattering data (important for deriving cross-sections needed to explain structural features at surfaces, adsorption-desorption phenomena, and diffusion). The work in lattice dynamics being pursued by Fano provides this thrust with computational models that allow surface force fields to be derived from inelastic helium and electron scattering measurements, nicely complementing the electronic structure work of Burdett on adparticle interactions. Finally, Mazenko's work completes this area, providing needed information on two-dimensional ordering dynamics. The third and final topical area in this thrust is concerned with the structure and dynamics of complex molecular films. Rice's efforts in this area have evolved from studies of the liquid-vapor interface to include theoretical and experimental work on the structure and properties of complex amphiphile molecules supported on liquid surfaces, and of polymers at liquid and solid surfaces. The activities on polymer dynamics have been pursued in conjunction with theoretical efforts by Freed. These theoretical efforts have been strengthened with the addition of Witten's expertise in the area of macromolecular dynamics.

Taken in total, Chicago's Surface Dynamics Thrust seeks to develop an improved molecular level understanding of interfacial phenomena over the range from relatively "simple" atomic adsorbates

up to complex molecular systems. The following gives highlights of on-going work in this area.

I. ADPARTICLE DYNAMICS AND SURFACE REACTIVITY

A. SURFACE DIFFUSION

In this area work consisted of diffusion anisotropy measurements by Gomer and co-workers for CO on Ni(111) and Ni(115), ^1H and ^2H on Ni(111), and W diffusion on W(211) and several stepped surfaces. Realizing the important role that surface phonons play in diffusion, Gomer and Sibener have begun identifying systems for study in Sibener's inelastic helium and inelastic electron scattering laboratories. The Ni(111) measurements are being complemented by Sibener and Fano's surface phonon work on this surface.

(i) Field Emission Fluctuation Measurements

Surface Diffusion CO on Ni(111) and (115)

T.S. Lin, H-J. Lu and R. Gomer have investigated these systems by the field emission fluctuation method.¹ On Ni(111) there is little coverage dependence of diffusion, with $E_d = 6.9$ Kcal, $D_0 = 10^{-3}\text{cm}^2\text{sec}^{-1}$ except for a spike in D_0 at CO/Ni ~ 0.4 . This is so despite a strong variation with coverage of $\langle(\delta N)^2\rangle/N$, which is the inverse of the so-called thermodynamic factor, $(\partial\beta\mu/\partial\ln\theta)_T$. Here N is the mean particle number in the probed region, μ chemical potential, $\beta \dots (k_B T)^{-1}$ and θ coverage. The diffusion coefficient D can be written as

$$D = (\partial\beta\mu/\partial\ln\theta)_T a^2 \Gamma(\theta) e^{-\beta E_d(\theta)} \quad (1)$$

where $\Gamma(\theta)$ is an effective attempt frequency, a the mean jump length and $E_d(\theta)$ an effective activation energy. Our results indicate that

there is an apparent compensation between changes in $(\partial\beta\mu/\partial\ln\theta)_T$ and $\Gamma(\theta)e^{-\beta E_d(\theta)}$. The E_d value obtained in the present work agrees very well with that found by Shen and co-workers² by an entirely different method, although our D_0 values are two orders of magnitude larger than the Shen et al. value.

On Ni(115) E_d and D_0 vary with coverage: $E = 6$ Kcal for $\text{CO/Ni} \leq 0.6$ and 4 Kcal for $\text{CO/Ni} \geq 0.6$. $D_0 \sim 10^{-3}\text{cm}^2\text{sec}^{-1}$ at low and $\sim 10^{-5}\text{cm}^2\text{sec}^{-1}$ at high coverage. Again there is a strong increase in $\partial\beta\mu/\partial\ln\theta$ with increasing coverage which is not manifested in the variation of D with coverage. The activation energies and their variation with θ agree quite well with the results of White and co-workers on Ni(100) obtained by the LID method.³ Since Ni(115) consists of terraces of (100) orientation this agreement is interesting, since it indicates that closepacked steps do not impede CO diffusion. This is also substantiated by the fact that the long time behavior of our correlation functions indicates 2-dimensional diffusion.

^1H and ^2H on Ni(111)

T.S. Lin and R. Gomer are investigating this system. To date only diffusion in the activated regime has been studied. Activation energies are 3.2 Kcal, independent of coverage or isotope. $D_0 \sim 10^{-5}\text{cm}^2\text{sec}^{-1}$ at low and $\sim 10^{-6}\text{cm}^2\text{sec}^{-1}$ at high coverage independent of isotope. This behavior contrasts with that on W(110) where D_0 increased with coverage and mass.⁴ The reasons for the behavior of D_0 on Ni(111) are not yet understood.

Diffusion of W on a W(211) Plane

The diffusion of W on a (211) plane of a W field emitter has been reexamined by D.S. Choi and R. Gomer by means of the fluctuation autocorrelation method. Diffusion along channels yielded $E = 16.8 \pm 0.5$ Kcal, $D_0 = (3 \pm 1) \times 10^{-5} \text{cm}^2 \text{sec}^{-1}$. $E = 6.6$ Kcal, $D_0 = 4 \times 10^{-9} \text{cm}^2 \text{sec}^{-1}$ for diffusion across channels at $T < 752$ K, and $E = 24$ Kcal $D_0 = 5 \times 10^{-4} \text{cm}^2 \text{sec}^{-1}$ at $T > 752$ K. The results for diffusion along channels yield E and D_0 values intermediate between recent results by Wang and Ehrlich⁵ using field ion microscopy ($E = 19$ Kcal, $D_0 = 7.7 \times 10^{-3} \text{cm}^2 \text{sec}^{-1}$) and Tringides and Gomer,⁶ using the same method as the present work but a larger slit ($E = 13.3$ Kcal, $D_0 = 7 \times 10^{-7} \text{cm}^2 \text{sec}^{-1}$). The results for cross channel diffusion are in good agreement with those of Tringides and Gomer below 752 K, where these authors stopped. The new high temperature results suggest that the channel wall exchange mechanism postulated by Tringides and Gomer for cross channel diffusion at low T gives way to diffusion by climbing over the channel walls with higher E but also higher D_0 above 752 K. This work is in press.⁷

Diffusion of Tungsten on Stepped Tungsten Surfaces

D.S. Choi, S.K. Kim, and R. Gomer have investigated the self diffusion of thermally generated tungsten atoms near (123) and (257), on the zone (011)-(112) and on (023), on the zone (011)-(001) of a tungsten field emitter by the field emission fluctuation method, using a rectangular probe in order to investigate diffusion anisotropy. In agreement with earlier findings⁸ diffusion of single W atoms along and across (011) terraces separated by (011) steps, i.e. step edges

running along $[111]$ is essentially isotropic with $E_d = 16$ Kcal, $D_0 \sim 10^{-4} \text{cm}^2 \text{sec}^{-1}$, while atoms can cross (001) oriented steps only with much higher activation energy $E_d \sim 35$ Kcal, $D_0 = 10^{-2} \text{cm}^2 \text{sec}^{-1}$. Slow diffusion parallel to steps attributed previously⁸ to kink motion was also seen along the zone (011)-(112) but seems more complicated than previously assumed, with several regimes, which may correspond to motions of different kink configurations. Distinct dips in the slow regime diffusion coefficients occurred at 910 K, somewhat higher than the previously seen⁸ onset of dips, 875 K, and may indicate roughening, as previously hypothesized. Slow diffusion perpendicular to steps was also seen in this zone and is not fully understood. It may arise from some step components always perpendicular to the short slit dimensions, or may correspond to more complicated surface configurations than the step and terrace pattern on an ideal emitter surface.

(ii) Diffusion on Surfaces-Theory

The experiments of Gomer on the diffusion of hydrogen atoms on the tungsten 110 surface display a remarkable array of phenomena.^{9,10} Foremost among these is perhaps the large isotope effects on the hydrogen diffusivity. For instance, in the limit of zero hydrogen coverage the diffusion is observed to proceed by tunneling for temperatures $T < 100\text{K}$ and to be thermally activated for $T > 125\text{K}$. The activation energy is 4kcal/mole with an isotope dependence of no more than 0.1kcal/mole. The Arrhenius prefactor D_0 , however, increases by three orders in magnitude in going from H to D and another two orders of magnitude from D to T. This enormous isotope

inverse isotope effect has been exhibited in previous reports where $\ln D_0$ is found to be proportional $M^{-1/2}$, with M the hydrogen isotope mass. The unusual plot is motivated by the theory¹¹ of Freed that is described below.

Simple models of tunneling lead to the expectation that the tunneling diffusion should depend exponentially upon $-(M)^{1/2}$, but extrapolations using H and D yield a T tunneling diffusion constant off by six orders of magnitude.¹⁰ A theory of this enormous isotope effect has been given by Freed and Gomer¹² using the same model introduced by Freed to explain the isotope effect on the thermally activated diffusion. Oxtoby¹³ has used the same model to study the crossover between the tunneling and thermally activated regimes and to explain the increased range of the crossover regime as the mass of the hydrogen isotope is increased.

The theory of these fascinating phenomena invokes a separation of time scales between the rapid hydrogen motions and the slower tungsten motions.^{11,12} This quantum mechanical model marks an important departure from the classical mechanical theories that have customarily been used to describe thermally activated diffusion, and it introduces new features in the treatment of the tunneling. The model consists of the hydrogen vibrations coupled to local phonons as described by an Einstein model.

The thermally activated diffusion requires stepwise excitation of the hydrogen vibrations whose frequency greatly exceeds that of the phonon modes. Thus, the huge inverse isotope effect on the thermally activated diffusion emerges as another example of an energy gap law for multiphonon processes (the excitation of hydrogen

vibrational quanta by several phonons.) Freed and Gomer provide one mechanism for the observed anomalous isotope effect on the tunneling as due to the dependence of the local phonons, and therefore of the Franck-Condon factor for the phonons, on the hydrogen mass that arises from the Born-Oppenheimer like time scale separation.¹² The experimental data for both the tunneling and the activated regions have been combined with the theory to extract independent estimates of the hydrogen-phonon couplings, and both independent estimates agree to within an order of magnitude,¹² demonstrating the consistency of this simplest model and suggesting circumstances in which the isotope effects are anticipated to be much smaller.

B. ADSORPTION AND DESORPTION

Much of the activity in this area has centered on the adsorption-desorption behavior exhibited by thin film systems, and how the properties of such systems vary with film thickness. Metallic overlayers have been studied in Gomer's group, with the properties of Cu overlayers on W(110) receiving particular attention. During the coming year Sibener's group hopes to construct and install metallic dosers of the type designed by Gomer in their inelastic electron scattering instrument, and to initiate complementary measurements on multilayer metallic films. His group has also initiated studies of coverage dependent desorption phenomena, beginning to address how inter-adsorbate interactions influence adparticle-surface interactions. Sibener's group is also continuing studies of resonantly induced laser photodesorption from physisorbed thin film systems.

Freed and co-workers will initiate theoretical work on surface photodesorption and photodissociation dynamics, which should nicely complement the above experimental effort.

(i) Adsorption, Desorption, Electron Induced Processes

Adsorption, Desorption and Dissociation of N_2 on W(110)

J.C. Lin, N. Shamir, and R. Gomer investigated this system, an interesting example of weak molecular chemisorption, which can also lead to dissociative adsorption. N_2 adsorbs molecularly on W(110) at $T_s \leq 100$ K with high and nearly constant sticking coefficient ($s \sim 0.7$). Saturation coverage is estimated as $N_2/W = 0.7$, from the $p(4 \times 1)$ LEED pattern seen at saturation and by analogy with CO adsorption. Desorption at ~ 130 - 150 K seems to occur from more than a single binding state, even for partial coverages. The tightly bound component (75% of total N_2 adsorbed, independent of coverage) desorbs with first order kinetics as shown by isothermal measurements with $E = 10.3$ Kcal, $\nu = 10^{15} \text{sec}^{-1}$. $\sim 10\%$ of total N_2 is converted to atomically bound N during desorption. The amount converted is independent of desorption temperature over the range 128 - 148 K, suggesting an activation energy equal to that of desorption of the tightly bound component, i.e. ~ 10 Kcal. This suggests that dissociation from preadsorbed N_2 occurs via a different channel than dissociation from impinging energetic N_2 molecules.

Electron Stimulated Desorption and Conversion of N_2 Adsorbed on a Tungsten (110) Plane

Q-J. Zhang, J.C. Lin, N. Shamir, and R. Gomer looked at the response of $\gamma - N_2$ on W(110) to electron impact. The desorption products are principally neutral N_2 and small amounts of neutral N, which may come from decomposition of N_2 in the mass analyzer. N_2^+ was not detected. N^+ is seen for electron energies above 60 eV. Approximately 32% of the initial saturated $\gamma - N_2$ layer (in terms of N atoms) is converted by electron impact to chemisorbed atomic N at $E_- = 150$ eV, corresponding to $N/W \sim 0.50$. It was possible, by thermal desorption after electron impact for different times to follow both the appearance of N and the desorption of N_2 . It turns out that the cross section for conversion to adsorbed atomic N is $2.5 \times 10^{-18} \text{cm}^2$, virtually independent of N_2 coverage remaining. The ESD signal for N_2 is not proportional to the amount of N_2 remaining on the surface. The data indicate that along with desorption there is conversion to a electron impact desorption inactive state (not atomic N) which however is either N_2 or desorbs thermally like N_2 . UPS measurements show that such a new molecular state, with 5σ 1π shifted to higher binding energy by ~ 1 eV is formed by electron impact. The desorption cross section is $1 \times 10^{-17} \text{cm}^2$, the conversion to inactive N_2 , $8.5 \times 10^{-18} \text{cm}^2$. The threshold for N_2 desorption is $E_- = 7-8$ eV, suggesting creation of a $5\sigma^{-1}$ state as the desorption mechanism near threshold. Conversion to adsorbed N occurred at $E_- \geq 12.5$ eV within our detection limit (XPS of the N 1s level of atomic N) suggesting a low energy intramolecular N_2 excitation. N^+ is not formed from chemisorbed N but by Coulomb explosion of N_2 ,

probably after creation of a $3\sigma^{-2} 2$ hole state. The weak binding of N_2 and the resultant large N_2 -W separation are postulated to account for the absence of N_2^+ . At the large N_2 -W distance in the ground state vertical transitions lead to the attractive part of any ionic curves reached, so that N_2^+ is propelled toward the surface and neutralized before it can desorb as an ion. Similarities and differences with the ESD behavior of CO are rationalized in terms of the differences in 5σ and 2π orbital distributions in the two cases.

Electron Stimulated Desorption from CO and O Adsorbed on Clean and Cu Covered W(110) Surfaces

J.C. Lin and R. Gomer also investigated electron stimulated desorption from CO adsorbed on $Cu_n/W(110)$ with $n = 0, 1$, and 2 in order to compare cross sections and thresholds for CO, CO^+ , and O^+ desorption. It was found that the thresholds for all three products were virtually independent of the presence or absence of Cu, indicating very similar mechanisms; however cross sections for $n = 1, 2$ were appreciably higher than on clean W(110). The threshold for CO production is attributed to creation of a 5β hole; absence of $2\pi_b$ DOS for $n \geq 1$ rules out a $2\pi_b \rightarrow 2\pi_a$ transition as the mechanism. CO^+ formation near threshold may occur by creation of a $5\beta^{-2}$ state. Arguments are presented to show that formation of $4\beta^{-1}$ also corresponds to the CO^+ threshold and may lead to CO^+ desorption. O^+ production from adsorbed CO corresponds to formation of various 2 hole states. Comparison of yields of neutral CO from $n = 0$ and $n \geq 1$ also made it possible to obtain desorption and β^- CO conversion cross sections for CO adsorbed on bare W(110).

The ESD behavior of $\text{O/Cu}_n\text{/W(110)}$ layers for $n = 0,1-4$ was also investigated. Only O^+ could be detected in all cases and there was no change in O coverage after prolonged electron bombardment. It is argued that O^+ comes from minority states corresponding to O adsorption on edge or corner metal atoms at steps and other imperfections. The thresholds are consistent with initial creation of a 2s hole on O, followed by filling of this hole by a metal electron and ejection of an O 2p Auger electron. The resulting $\text{M}^+ - \text{O}^+$ state leads to desorption of energetic O^+ . This process restricted to O bound to metal atoms in sufficiently poor contact with the rest of the substrate to give M^+ and O^+ the required lifetimes.

None of the processes investigated showed openings of new channels at energies corresponding to creation of holes in substrate metal atoms. This work has been published.¹⁴

Adsorption of Pd on O/W(110) and CO/W(110)

In a previous investigation¹⁵ N. Shamir, J.C. Lin, and R. Gomer found that Cu monolayers adsorbed on O/W(110) or CO/W(110) showed metallic properties, presumably because of formation of a partially filled s-band, capable of screening. These workers have now looked at adsorption of Pd. On O/W(110) rather disordered Pd overlayers are formed and do not show strong metallic properties, i.e. do not screen the W-O dipole potential very much. Pd adsorption on CO/W(110) seems to occur even at 90 K with rearrangement so that most CO is on top of or next to Pd, with Pd not forming an overlayer on CO. This behavior is in sharp contrast to that previously reported for Cu adsorption on the same surfaces. Metallicity is probably absent because Pd atoms have a $4d^{10}$ configuration and are unable in a single

layer to form a partially filled band, or do not have enough overlap to behave as other than isolated atoms.

Adsorption of CO on Pd₁/W(110)

In a previous investigation Chelvayohan and Gomer¹⁶ found that CO adsorption on Cu₁/W(110) showed very unusual thermodynamic and kinetic properties. These were attributed to the fact that Cu, while pseudomorphically adsorbed on W(110), has considerable "slop", being some 10% smaller than W, so that adsorption on Cu₁/W(110) can lead to Cu rearrangement. This was manifested by large entropy as well as enthalpy changes with coverage including a rather unusual phase transition at half coverage, marked by a sudden drop to zero in the isosteric heat of adsorption, and a corresponding near-divergence in the differential surface entropy. Zhao and Gomer have carried out comparable experiments for CO on Pd₁/W(110) to see if such effects would be absent in a system in which the size of the metallic adsorbate matches that of tungsten. There are no real anomalies either in ΔH or S , supporting the hypothesis that the behavior seen for Cu₁/W(111) is related to the size mismatch between Cu and W.

(ii) Desorption Dynamics of Molecular Overlayers

In an attempt to begin assessing how internal degrees of freedom couple to the temperature both during thermal desorption Padowitz and Sibener¹⁷ have examined the sublimation dynamics of NO films physisorbed on an Ag(111) substrate. Rotational and angular distributions were measured. They found that NO molecules

subliming into vacuum from a condensed NO film at 50 K exhibit cosine singular flux and Boltzmann rotational distribution at the surface temperature. This implies that the sticking probability for incident molecules is independent of angle or rotational energy, at least for levels populated at 50 K. Several models for rotational distributions of desorbing molecules were examined. The extent to which desorption can be used as a probe of the surface dynamics of condensed phases was also considered in this work. The results touch on issues fundamental to obtaining microscopic dynamical information for non-equilibrium interfaces. Work is continuing on using desorption to probe the microscopic dynamics of gas-surface interactions.

(iii) Coverage Dependent Interaction Potentials

New efforts in Sibener's multiple beam scattering laboratory are examining how gas-surface potentials vary as a function of adsorbate density. Measurements by Padowitz, Peterlinz, and Curtiss on CO, O, and H interactions with Rh(111) are being pursued. A new *three* molecular beam arrangement is being used which allows a steady state adsorbate coverage to be established; and then *weakly* perturbed with a gaseous pulse. Helium scattering is being used to temporally monitor the time evolution of adsorbate coverage following short (weakly perturbative) pulses of reactants. Initial work on CO is indicating high signal-to-noise signals are accessible. Arrhenius plots at several positions in the adsorbate phase diagram will be generated. The information so obtained is of high interest to Burdett, Gomer, and Freed who are examining adparticle interactions.

(iv) Laser Induced Desorption - Resonant Excitation

Relatively little information currently exists on the rates at which energy migrates between molecular vibrational modes, molecule-surface modes, and the surface for vibrationally or electronically excited molecules which are adsorbed on well-defined substrates. Resonantly excited desorption experiments can in principle address some of these questions.¹⁸⁻²² One of the crucial points is to determine whether optically induced adsorbate desorption (and thin film ablation) proceeds via resonantly induced predesorption (direct channel) or by resonantly induced heating of the surface region. Sibener's group has set up such a research effort to explore the dynamics and energetics of both photodesorption and adsorbate photodissociation. The quantum yields of various photoprocesses as a function of distance from the surface (using inert gas spacers) are also being explored. Discussions on the theoretical description of resonant photodissociation processes and continuing between the Sibener and Freed research groups.

To date, the experiments have centered on probing the angular distributions, velocity distributions, and internal state distributions of NO desorbing from thin films of NO adsorbed on a Ag(111) substrate.²³ It has been shown that ultraviolet laser induced desorption from the surface of a thin nitric oxide film proceeds via two mechanisms which are present simultaneously. One mechanism is attributed to laser induced thermal desorption while the other is due to a non-thermal, single photon process. Translational energies of desorbed molecules were measured from time-of-flight (TOF) spectra

taken with a mass spectrometer, while the internal energy distribution of molecules desorbed in the non-thermal channel was determined by a (1+1) -resonance enhanced multiphoton ionization (REMPI) probe. NO monomer in the $^2\Pi_{3/2, 1/2}$ electronic ground states was the only significant product. There were two distinct characteristic TOF components, which Sibener and co-workers associate with different desorption mechanisms. Each component had a different velocity and angular distribution, and their relative yields varied with laser pulse energy and NO layer thickness. Under conditions where both mechanisms gave comparable desorption yields, they obtained TOF distributions which were bimodal. A "slow" peak with an average translational energy up to .06 eV was Maxwellian with temperatures between 160 and 280 K and a broad angular distribution. Yield in this peak increased strongly with layer thickness and exponentially with laser pulse energy. A "fast" TOF peak with average energy of 0.22 eV was non-Maxwellian, with an angular distribution peaked toward normal, and yield increasing linearly with laser pulse energy. REMPI of the fast peak showed a vibrational population ratio $v=3:v=2$ of 0.85. A Boltzmann plot of the rotational population distribution of $v=2$ molecules, if fit with a single line, gave a temperature of 2500 K. These angular, velocity, rotational and vibrational distributions are being studied to suggest mechanisms for the non-thermal desorption.

(vi) Laser Induced Desorption: Non-resonant Excitation

This new initiative headed by Levy is intended to elucidate the mechanism by which large, fragile molecules are laser desorbed from

surfaces without extensive fragmentation. Since the total binding energy of these molecules to the surface can be larger than the dissociation energy of the molecule, the desorption of intact molecules is striking and unexpected. Research is designed to measure the internal and kinetic energy distributions of the desorbed molecules with the hope that the desorption mechanism can be inferred from a detailed description of the desorbing molecules. Our accomplishments during the past year fall into two categories. First, we have continued to investigate the gas phase spectroscopy of the molecules that we will want to study in the laser desorption experiments. The internal energy distributions of the desorbed molecules will be inferred from their two-photon ionization spectra, and an understanding of these spectra is essential for converting the raw data into the desired energy distributions. Second, we have designed and have begun construction of the apparatus that will be used to make the measurements on the laser desorbed molecules. Since this instrument is a cross between a surface science apparatus and a molecular beam spectrometer, our design work has greatly benefitted from collaboration with Sibener.

During the last year we have continued our spectroscopic studies of amino acids, peptides, and related molecules to improve our understanding of the vibrational and rotational levels in these molecules. We have used laser desorption to produce supersonic molecular beams of peptides and have obtained high resolution gas phase fluorescence excitation and dispersed fluorescence spectra of these species.²⁴ The fluorescence spectra of small tryptophan-containing peptides such as trp-gly, gly-trp, trp-gly-gly, and gly-gly-

trp have been observed in a molecular beam. In general, we see several conformers of each peptide and, as in the case of the single amino acid tryptophan, one of the conformers in each peptide has special properties. The absorption spectra of all conformers are sharp, and while the emission spectra of most of the conformers are also sharp, the emission spectrum of the special conformer is broad and red shifted. This broad emission resembles emission from an exciplex, and we have produced a model which says that in the special conformer, an intramolecular exciplex is formed between the indole chromophore and the peptide backbone. Experiments with derivative molecules indicate that a hydrogen bond in the peptide backbone produces one highly polar conformation, and the interaction of the backbone dipole moment with the indole chromophore produces the intramolecular exciplex. There are known to be two low-lying excited electronic states of indole, the ^1L_a and the ^1L_b , and the energy of the ^1L_a is known to have a large dependence on the environment. In a polar environment, the energy of this state is lowered below that of the ^1L_b state, and we believe that this is the interaction that produces the exciplex-like emission. The spectroscopic work on peptides is being done by Mike Tubergen, a graduate student, with partial MRL support.

The design of the laser desorption apparatus is nearly complete and construction has now begun. The laser desorption instrument will have a sample film deposited on a movable and coolable stage. Molecules will be desorbed by 10 nsec pulses from a doubled Nd:YAG laser, and the desorbed neutrals will be allowed to drift into a time-of-flight mass spectrometer. They will then be resonantly ionized by

a tunable ultra-violet laser. The intensity of the ion beam as a function of the time delay between the desorption and ionizing lasers will provide a measure of the kinetic energy distribution, while the intensity as a function of ionizing laser frequency will provide a measure of the internal energy distribution. After ionization, the ions will be accelerated through a flight tube to a position sensitive detector. The delay between ionization and detection will measure the mass of the ion, and the position of the ion on the detector will provide the angular distribution of the neutrals that were desorbed from the surface.

Design of the apparatus was greatly aided by a computer-aided drawing program and an ion trajectory simulation program. These were used to design the main vacuum chamber, the pumping stack, the sample translating and cooling stage, the ion and laser optics, and the detector. We have now taken delivery of the pumps and associated vacuum hardware, the main chamber, the dual microchannel plate ion detector, and the computer that will run the experiment. The Nd:YAG laser to be used for desorption is on order, and remaining vacuum hardware and ion optics are under construction in our machine shop.

C. SURFACE REACTION DYNAMICS

(i) Multiple Source Modulated Molecular Beam Reactive Scattering Applied to Complex Reaction Kinetics at Surfaces

A major recent innovation in Sibener's laboratory has been the successful implementation of a **three** molecular beam reactive

scattering arrangement in our laboratory. Brought to fruition by D.F. Padowitz, this is allowing Sibener's group to: i) study surface reactions under arbitrarily chosen and constant adsorbate coverage conditions -- important for elucidating the coverage dependence of activation energies and pre-exponential factors ii) **linearize** surface kinetics by operating in a very weak modulation limit and iii) avoid the near-zero coverage regime in which reactive scattering experiments are occasionally forced to operate. For example, if we currently wanted to study the reaction $X + Y \rightarrow Z$ we would use one continuous molecular beam X, modulate the second Y, and monitor the time evolution profile of Z. This has the disadvantage that the concentration of Y on the surface varies over a wide range during each modulation cycle. Furthermore, this "deep" modulation scheme can also induce time dependent behavior in species X, and other reaction intermediates. One of the consequences of this (typical) method is that the measured reaction rate is a convolution over all coverages of Y on the surface. This new arrangement allows us to have two continuous beams, X and Y, and a third modulated probe beam Y(t). Now the continuous Y beam can ideally be used to fix the steady state concentration on the surface at a specific point. The modulated Y(t) beam can then be used to "dither," (i.e., **weakly perturb**), the concentration around the preselected steady state value if its intensity is much lower than that of the continuous beam. A simple test to see if linearization has been experimentally realized is to see if the even harmonics vanish in the Fourier transform of the product time evolution waveform when the system is driven by a purely odd chopper function. This limit has now been accomplished

for the simple $\text{H}_2 + \text{D}_2 \rightarrow \text{HD}$ and the more complicated $\text{H}_2 + \text{D}_2 + \text{O}_2 \rightarrow \text{HDO}$ reactions. To summarize this important accomplishment: Padowitz and Sibener have successfully demonstrated that the coupled differential equations that describe elementary reaction steps can be linearized, allowing perturbation theory to be used to extract kinetic and mechanistic information under *arbitrarily chosen* surface coverage regimes. Furthermore, this technique can, under favorable conditions, allow us to isolate the kinetics for selected elementary reaction steps.²⁵ This has been accomplished using a novel three beam scattering arrangement. Specific results include isolating the $\text{O} + \text{H} \rightarrow \text{OH}$ intermediate step in the water synthesis reaction, finding $E_a = 2.5$ kcal/mole for the $\text{H} + \text{D} \rightarrow \text{HD}$ reaction at low coverage.

(ii) $\text{CO} + \text{O}_2/\text{Rh}(111)$

During the past grant period Sibener's reactive scattering program has also given attention to the catalytically important $\text{CO} + \text{O}_2/\text{Rh}(111) \rightarrow \text{CO}_2$ reaction.^{26,27} In particular, angle-resolved modulated molecular beam scattering experiments have been used to investigate the kinetics and mechanism of this reaction. Experiments were performed under conditions where the oxygen atom coverage was high, and the CO coverage was near zero. Under these conditions pseudo first order kinetics were observed. The reaction was found to have an activation energy of 24.5 kcal/mole and a pre-exponential factor of $1.9 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. The angular distribution of the product CO_2 was sharply peaked about the surface normal, and could not be described by a simple $\cos^n \theta$ expression. One of the primary findings of this study was that no evidence for a branched reaction mechanism

was seen in Fourier analysis of the product time-of-arrival waveforms, and that waveforms obtained at different desorption angles from the surface normal were indistinguishable. (Such a branched mechanism might have been inferred from the data, if the only information came from the product's angular distribution, with one channel being associated, for example, with the $\cos^2\theta$ term of the angular distribution, and another channel with the $\cos \theta$ term.) "Surface transfer functions" obtained by plotting the real part vs. the imaginary part of the Fourier transform of the appropriate CO_2 time-of-arrival waveforms.²⁸ It has been well established that this method is quite sensitive to qualitative features of the reaction mechanism.^{29,30} Various types of mechanisms, such as simple first order reactions, parallel or sequential reaction networks, higher order kinetics, or diffusion controlled reactions, have all been shown to produce a distinctive pattern in the transfer function.³¹ Our conclusions point out the importance of collecting product angular, residence time, and velocity information during studies of surface reaction mechanisms.

The data presented thus far do not suffice, however, to rule out a branched mechanism entirely. In the limit of two branches with identical rate constants, it would clearly be impossible to distinguish between them. Since relaxation at the surface may proceed on a very short time scale, the difference in surface lifetime between molecules which equilibrated and those which desorb directly might be smaller than the detection limit ($\sim 10^{-4}$ seconds for the chopping frequencies used here). Further evidence for a single mechanism has been found in preliminary measurements of the velocity distributions in the

product CO_2 molecules. Even at an angle of 60° from the surface normal, non-thermal velocity distributions with translational energies in excess of those corresponding to the surface temperature were obtained, indicating that the molecules desorb without equilibrating in the CO_2 adsorption well. Furthermore, no evidence was seen for a bimodal velocity distribution, as would be expected to arise from the sort of two-channel mechanism suggested by Segner, et al.³²

(iii) Catalysis on Bimetallic Surfaces

The essence of heterogeneous catalysis is the reduction of activation energies of reactions. In heterogeneous oxidation or hydrogenation a prerequisite is of course the splitting of the O-O or H-H bond by dissociative adsorption which is generally unactivated. In addition the reaction partner must be bound to the surface tightly enough to have a reasonably high surface concentration during reaction, but not so tightly as to inhibit reaction by making its activation energy too high. Finally reaction products must be adsorbed weakly enough to desorb and not block the surface. Additionally at least one of the reactants must be mobile enough under reaction conditions to find the other.

During the past Grant period it was found that the heat of adsorption of CO on $\text{Pd}_1/\text{W}(110)$ is 24-12 Kcal, depending on coverage as shown in the Accomplishments section. This is considerably less than the heat of adsorption on bulk $\text{Pd}(111)$, 34 Kcal/mole.³³ Our work on O/Pd segregation also showed that O_2 is largely adsorbed as O atoms. Thus the possibility exists that a $\text{Pd}_1/\text{W}(110)$ surface might catalyze CO_2 formation at much lower temperatures than bulk

Pd(111), 300- ~ 500 K (7). We have taken a preliminary look at this reaction and find that CO₂ formation (or more precisely desorption) occurs below 200 K. Although Conrad, Ertl, and Küppers³³ have reported some CO₂ formation at high CO coverage on Pd(111) our preliminary results show this to be true even at low CO coverages, and also show interesting differences between oxygen and CO coadsorption at 25 K and 90 K. Since we have also found in the current grant period that Cu or Pd and oxygen or nitrogen coadsorbed on W(110) segregate at high temperatures, there are clearly limits on the useful stability range of such systems, but it is still worthwhile to explore them further.

II. SURFACE PHONON SPECTROSCOPY AND GAS-SURFACE INTERACTIONS

This part of our MRL Surface Dynamics Thrust involves close collaboration between the experimental group headed by Sibener and the theoretical efforts led by Fano, Light, Burdett, and Mazenko. The Sibener team is currently active in inelastic electron and helium surface scattering, as well as elastic helium diffraction. The Fano group brings to this effort lattice dynamics and quantum electron scattering calculations. Light and co-workers are active in the area of neutral particle-surface scattering calculations. Electronic interactions between adparticles, and for clean surfaces, are being examined by Burdett. Mazenko bring his expertise in ordering kinetics in three and two dimensional systems to this thrust. His work on bulk Cu₃Au behavior may become especially valuable as Sibener's group starts to examine the surface ordering kinetics of this fascinating alloy. The

information extracted on surface force fields and surface vibration in this section is also of great importance to the work of Gomer and Freed on surface diffusion. For example, at the present time Gomer and co-workers are studying adsorbate diffusion on flat and stepped Ni surfaces which Sibener and Fano's group are tackling the vibrational behavior of these interfaces.

A. ELASTIC AND INELASTIC HELIUM SCATTERING

During the past grant period Sibener's research group has continued to use angle and velocity resolved inelastic helium scattering to study the spectroscopy of surface phonons. These measurements are being supported by theoretical contributions from Light (scattering theory) and Fano (lattice dynamics). Such experiments allow one to directly examine the dynamical properties of clean and adsorbate covered surfaces, much in the way that inelastic neutron scattering has been used in the past for determining the vibrational properties of bulk materials. Of the surface vibrational probes that are currently available, inelastic helium scattering is the best suited for examining low energy collective excitations since it has excellent energy resolution ($\Delta E \sim 250 \mu\text{eV}$), high surface specificity, and momentum sufficient for probing excitations across the entire surface Brillouin Zone (SBZ). Work on the dynamical properties of ordered rare gas monolayers and multilayers has been completed, culminating in the publication of three highly detailed manuscripts on this topic.^{34,35,36} Tight coupling between Sibener and Light was essential for the success of this project. These studies have revealed in a very straightforward manner how the

surface vibrational modes of an atomically thin rare gas film evolve, on a layer-by-layer basis, into those of a thick crystal. Lattice dynamics calculations have been compared with the experimental results in order to assess the extent to which various potential terms contribute to the vibrational properties of these thin films.^{3,7} Quantitative agreement between theory and experiment has been found for most of the dispersion curves. Attention has now shifted to the structural and dynamical properties of intermetallic surfaces, with $\text{Cu}_3\text{Au}(001)$ keeping the system under examination.

(i) $\text{Cu}_3\text{Au}(001)$

During the past year Sibener's inelastic single phonon helium scattering work has been fully shifted to his new high resolution scattering laboratory. The focus of this inelastic helium scattering work has recently been on the $\text{Cu}_3\text{Au}(001)$ system. This surface undergoes a fascinating substitutional disorder phase transition near $T_c \approx 660$ K, above which the Cu and Au atoms become randomly mixed on a face centered cubic lattice. They have succeeded in mapping out the surface phonon dispersion curves, i.e. vibrational frequencies as a function of phonon wavevector, for both the acoustic and optical modes across the surface Brillouin zone. The time-of-flight measurements are being interpreted with the help of an in-house written lattice dynamics code. The theoretical efforts of Knipp and Fano have been essential to the success of this project. Note that high quality superlattice diffraction spots are easily seen at 300 K and up to T_c for the ordered alloy phase, indicating that the initial inelastic scattering measurements correspond to a highly ordered

sample. Elevated temperature runs are now in progress in the vicinity of T_c , the disordering point for the alloy. So far, two surface phonon dispersion curves have been measured. The lower curve is the Rayleigh mode, whereas the upper curve is probably best described as the optical or folded Rayleigh mode. (Actually, the upper mode might be a surface resonance, rather than a truly localized surface mode.) Appropriate calculations are proceeding, using a slab technique (due to the inability of the Green's function approach to handle a polyatomic substrate) which allows for the possibility of surface softening, relaxation, and "rumpling." The bulk-phonon dispersion curves [as measured by inelastic neutron scattering]³⁸ of Cu_3Au reveal an assortment of force constants which are considerably more complicated than those of, for instance, bulk nickel. This makes the interpretation of *surface* phonon spectra that much more difficult, due to the resulting inevitable nonuniqueness of the surface force-field assignments. One possible fit incorporates realistic surface rumpling and uses bulk force constants for all of the near-surface interactions, with the exception of the Cu-Cu interlayer force constant, which is stiffened by 25%.

B. GAS-SURFACE INTERACTIONS

In these studies Sibener's experimental group, in conjunction with Light's theoretical effort, is using diffraction, selective adsorption, and rotationally inelastic scattering to probe the structure and interaction potentials (and hence surface charge density profiles) of clean and adsorbate covered surfaces. Excellent surface sensitivity is realized in these measurements as the classical turning points of

neutral particle trajectories occur just outside of the surface region. Valuable information on island size distributions, surface defect densities, physisorption interactions, and two-dimensional phase transitions can also be obtained from these experiments. Theoretical efforts directed by Burdett, Light, and Mazenko form a highly complementary component in this area. Light's quantum scattering calculations have proven to be essential in extracting information on interaction potentials from Sibener's elastic diffraction and selective adsorption measurements. Past joint activities between these two groups, sponsored by the MRL, have led to an improved understanding of molecular hydrogen interactions with metallic substrates, including spatially isotropic and anisotropic components of the potential.³⁹⁻⁴² Monolayer and multilayer rare gas crystals have also been examined.³⁶ The information obtained on how intermediate layers moderate the substrate's influence on surface properties as a function of distance are of central interest to Gomer's work on multilayer films. As stated previously, Sibener's group is now concentrating on scattering from ordered and disordered $\text{Cu}_3\text{Au}(001)$. Light's theoretical program is described below.

(i) Neutral Particle Scattering-Theory

Atomic beam probes of surfaces by Sibener's group permits investigation of the surface structure (e.g. ordered overlayers), the atom-surface soft corrugation potentials, the dynamical properties of the surfaces *per se* such as the surface phonon spectrum, and the dynamics of inelastic atom-surface processes via low energy phonon excitation, etc. Modeling of the atom-rigid corrugated surface

potential elastic scattering³⁶ via quantum close coupling calculations yielded substantial information on the potentials for the He-ordered rare gas overlayers. The analysis of the inelastic scattering, however, is necessary in order to obtain information on adsorbate-substrate interactions, phonon excitation processes, and atom-surface potentials.

During the past year Light and co-workers implemented a flexible discrete variable representation (DVR) for the scattering problem which permits an L^2 solution of the zero order elastic scattering problem. Although this approach has, to date, only been applied to reactive scattering in the gas phase,⁴³ it provides a very efficient framework for calculation of atom-surface scattering processes. In addition the calculation of rate processes by evaluation of the flux-flux autocorrelation function has been demonstrated for gas phase processes,⁴³ and conversion to deal with surface diffusion and thermal desorption of atoms and molecules is in progress.

C. INELASTIC ELECTRON SCATTERING-EXPERIMENT AND THEORY

(i) For Ni(111)

This research initiative is now underway in Sibener's new inelastic electron scattering laboratory. Funding for this facility was primarily obtained by Sibener from two different Department of Defense-University Research Instrumentation grants. The spectrometer is now fully operational. Initial measurements of W. Menezes and G. Tisdale on Ni(111) have been aimed at ascertaining how the properties (static and dynamic) of surfaces differ from bulk matter. These measurements are being complemented by the lattice

dynamics and quantum scattering calculations of Knipp and Fano. A publication is now in press⁴⁴ which reports experimental and theoretical results for Ni(111).

Specifically, the surface phonon dispersion relations for clean Ni(111) have been obtained along the Γ -M symmetry direction. The surface phonon spectra were obtained with Sibener's high resolution electron energy loss spectrometer (HREELS) operating in the off-specular impact scattering regime. Kinematic conditions were varied in order to selectively examine the Rayleigh mode and "gap" mode, as well as contributions from bulk phonons. Comparison of the experimental surface phonon dispersion relations and inelastic scattering cross sections with lattice dynamical and quantum multiple scattering calculations demonstrate that tensile surface stress is present at the level of 1.6 ± 0.2 N/m, and that the intraplanar surface force constant is $11 \pm 3\%$ softer than in bulk nickel. These conclusions were derived from Knipp's analysis of the surface phonon spectroscopy and inelastic electron scattering cross-sections for the Ni(111) system. A complete picture was obtained by measuring the Rayleigh mode (S_1) as well as the more elusive "gap mode" (S_2). This clean, unreconstructed, and close-packed surface has displayed *geometric* characteristics of "ideal termination." However, the surface phonon spectra exhibit *dynamic* aspects which differ distinctly from those predicted by a model that assumes the surface force constants to be identical to their bulk counterparts. Using the previously described numerical techniques, these "surface phonon anomalies" were reconciled in terms of two parameters: surface tensile stress of 1.6 N/m and intraplanar force-constant softening of 11%. These

numbers compare reasonably with those measured for similar transition metal surfaces. Unlike previous work, these conclusions were drawn from two different semi-independent methods, giving added confidence in our results. One method involved fitting the experimental dispersion curves to those corresponding to a theoretical lattice dynamical model. The other method involved fitting the *entire* calculated intensity, thereby taking into consideration the scattering from bulk modes as well as surface modes.

(ii) Surface Dynamics-Theory

Fano's theoretical research aims at complementing the high-resolution inelastic scattering experiments (e^- and He) performed by Sibener's group. The main participant in this research is Peter Knipp, a graduate student in the physics department. The goals achieved this year were manifold.

First was to develop a numerical tool to calculate the spectral density $\rho_{||}(\mathbf{Q}, \omega)$ of atomic oscillations near a crystal surface. This involves an exact, semi-analytic method sometimes referred to as the "Green's function approach." The program is designed to handle a broad family of surface-vibration problems, allowing for any combination of surface Miller-index, monatomic Bravais lattice, force-constant scheme, reconstruction, and adsorbates. Its only limitations are that the surface be commensurate with the substrate and that the vibrations be harmonic.

The Green's function approach⁴⁵ has considerable advantages over the more commonly-used, brute-force "slab technique."⁴⁶ For example, it facilitates the study of surface vibrations on high Miller-

index (i.e., stepped or "vicinal") surfaces. A numerical study of such surfaces has revealed a surprising new class of surface phonons, which are actually localized to the step edge.⁴⁷

One reason that the Green's function approach has been largely neglected is that, unlike the slab method, it does not yield the phonon eigenvectors $\vec{e}_l^{(n)}(\vec{Q})$ and frequencies $\omega_n(\vec{Q})$. Traditionally, such quantities have been used as critical inputs to vibrationally-inelastic electron⁴⁸ and helium⁴⁹ scattering calculations. However, an improved formulation of the problem has shown that the vibrational spectral density, which contains the phonon eigenvectors and frequencies through the combination

$$\vec{\rho}_{11}(\vec{Q}, \omega) = \sum_n \vec{e}_l^{(n)}(\vec{Q}) \vec{e}_l^{(n)*}(\vec{Q}) \delta[\omega - \omega_n(\vec{Q})]$$

can *also* be used as inputs to such scattering calculations, and in fact are more suitable.⁵⁰ This facilitates the treatment of scattering from bulk phonons as well as surface phonons. This work involved Burl Hall from the University of California at Irvine, a previous collaborator with the Sibener group.

Finally, on a subject which is related not to surface physics but instead to bulk properties, which interested Knipp and Fano at the outset of the association with MRL, Knipp has written a short comment on a paper which concerned itself with hydrodynamic modes in condensed materials ("Dispersion relation for collective modes in classical liquids and amorphous solids," Phys. Rev. A. - in press).

(iii) Theoretical Studies of Adsorbate Ordering on Surfaces

Studies using a variety of methods have established the presence of ordered arrays of ad-atoms on clean surfaces. (E.G. The work of Sibener and of Gomer). The observed pattern frequently depends on a variety of factors, such as the chemical identity of the metal, the face of the crystal on which adsorption occurs ((111), or (211) etc.) and the nature of the adsorbate itself. Sometimes it has been possible to understand these patterns in terms of the signs and relative magnitudes of the interaction potentials between neighbors of different types. Freed and Mazenko have worked on this problem. Gomer has shown that oxygen on tungsten (211) (bcc structure) finds itself in a situation where first nearest neighbors are attractive but second nearest neighbors are repulsive along the channels in the surface.

Burdett and co-workers are examining the variation in the magnitude and sign of the interaction using the moments method which we have used with considerable success to look at a wide variety of structural problems in molecules, solids, and surfaces. They are looking at a variety of adsorbate atoms and molecules attached to metal surfaces of different types and different geometries. In each case the results are being interpreted using the moments method and perturbation molecular orbital ideas which have found great utility in other areas of chemistry. The problem falls into the general area of structural order/disorder and the philosophy is similar to that used with Levin and Rosenblum in the area of high T_c superconductors, and with Newton, Kleppa, and Heinz in the area of oxides and sulfides. (Vide infra). Burdett's group is also starting to

look at the reconstruction of surfaces of interest to both Sibener and Gomer. Several results have been obtained in this area.

Burdett's effort has produced an extremely interesting analog of the 18 electron (or effective atomic number) rule found for molecules, in their studies on surfaces. The pair potential between two CO molecules (for example) attached to a single metal atom is small and negative (i.e. stabilizing) for a d^6 electron count and then jumps to a large positive value on the addition of more electrons. The magnitude of this pair potential exceeds the metal-carbon bond strength, and thus we expect the molecule to fall apart. (An example might be $\text{Fe(CO)}_6 \rightarrow \text{Fe(CO)}_5$). The electron count at which this pair potential becomes positive varies with the number and type of other ligands in the complex. On the surface, the most striking feature is the reduction in size of the pair potential (by two orders of magnitude) such that at an unfavorable electron count the energetic penalty is insufficient to eject an adsorbed atom or group. The electron count variation of the maximum in the pair potential varies with surface coverage in exactly the same way as it does in molecules.

We have also shown that there is a strong correlation between the activity of metal sulfides as hydrodesulfurization catalysts and the calculated pair potential between the sulfur atoms in the surface of the solid sulfide.* This suggests that it is the loss of sulfur from the surface to produce a defect which may be the rate determining step in this reaction. The experimental data for the first row metals show an activity plot with a smaller amplitude and peaking at a lower electron count than those for the second and third row metals. Both of these features are reproduced in our calculated pair potential by

recognizing that the first row metals give rise to high-spin and the heavier elements to low-spin systems.

We have also studied the ordering patterns of CO, and NO on nickel and have rationalized the observed strengthening of the metal-CO linkage as hydrogen is coadsorbed. Our calculations also show interesting results for CO, NO and CCH₃ on rhodium surfaces, and mimic the experimental results of Somorjai in this area. At present we are trying to unravel the electronic reasoning behind our results.

III. SEED AREA: STRUCTURE AND DYNAMICS OF COMPLEX MOLECULAR FILMS

Overview: For a number of years Rice has carried out theoretical and experimental studies of the structure of the liquid-vapor interface of a metal. These studies have involved the development of powerful theoretical techniques (e.g. self-consistent calculation of the electron density distribution, the effective ion-ion interactions and the ion density distribution in a Monte Carlo simulation of a many body system with electrons and ions) and utilization of state-of-the-art experimental methods (e.g. grazing incidence x-ray diffraction using a synchrotron source). The results obtained to date, in addition to their relevance to the determination of the structure and the composition of the free liquid metal surface, open the way to the study of how various contact media influence the structure and composition of the liquid metal-contact medium interface. One part of Rice's proposed research involves following up this line of investigation.

In the last two years Rice has initiated studies of the structure and properties of monolayers of amphiphile molecules supported on liquid surfaces, and of polymers at liquid and solid surfaces. Another part of Rice's proposed research involves further study, both theoretical and experimental, of the structural and dynamical properties of such systems. Freed had already been active in theoretical work on polymers at interfaces, and as a prelude to Rice's entry into this field, Freed trained one of Rice's graduate students in the theory of polymers at surfaces. The student then worked with Rice to develop theories to explain Rice's experiments and Monte Carlo simulations for these systems. Several of the new projects in this area will involve collaboration between Rice and Freed, while it is hoped that others will continue collaborations of Rice with Dutta and Ketterson (Northwestern MRL) and with researchers at Exxon.

These efforts in polymer interfaces and nanomolecular dynamics are further strengthened by the addition of Tom Witten to our MRL effort. Tom joined our physics faculty this year from Exxon. Sibener is also planning to join these efforts, with proposed inelastic electron scattering measurements on polymer films.

A. AMPHIPHILE MONOLAYERS

We have carried out self consistent quantum mechanical Monte Carlo simulations of the influence of a close packed monolayer of long chain amphiphile molecules on the longitudinal density distribution in the surface of supporting liquid metal.⁵¹ The results show that the monolayer-liquid metal interface has marked density oscillations extending several atomic diameters into the bulk liquid. The

principal source of the enhancement of the density oscillations is the stiffness of the monolayer; the field generated by the monolayer and the consequent electron density change, generate second order contributions to the enhancement of the density modulation. The existence of the density modulation in the liquid surface alters the thermodynamics of the monolayer and, conversely, the monolayer influences the electronic properties associated with the liquid metal surface, e.g. the work function for injection of an electron into the monolayer.

It has been found, unexpectedly, that rapid uniaxial compression of a monolayer of $C_{21}H_{43}OH$ ⁵² or of $C_{20}H_{41}COOH$ ⁵³ leads to generation of a metastable distorted hexagonal structure (probably with tilted molecules) in the region of thermodynamic state space where the hexagonal structure is stable. Then the uniaxial compression is stopped, and the surface pressure becomes isotropic, the distorted hexagonal structure transforms into the hexagonal structure via a nucleation mechanism. Shin and Rice⁵⁴ have investigated the theoretical basis for these observations. They have shown that the observed behavior is a consequence of nonzero tilt of the amphiphile molecules in the hexagonal phase, however small, since the projection of the molecular axis on the surface can be organized by the symmetry breaking uniaxial compression into a director, thereby lowering the chemical potential of the distorted hexagonal phase relative to that of the hexagonal phase when the uniaxial stress is present. Bohannon et al.⁵⁵ have shown, from grazing incidence x-ray diffraction data, that in the hexagonal phases of dense monolayers of $C_{21}H_{43}OH$ and $C_{20}H_{41}COOH$ on water the molecular axes

are tilted relative to the normal to the surface by of order 2° to 5° , in agreement with the theoretical analysis of the observed behavior under uniaxial compression.

Shin, Wang, and Rice⁵⁶ have generalized the Popielawski-Rice⁵⁷ theory of the low density monolayer equation of state to include the effects of interactions between the portions of the long chain amphiphile molecules outside the surface. They provide, for the first time, a consistent molecular interpretation of both the gas-to;-liquid expanded and the liquid expanded-to-liquid condensed phase transitions in the monolayer: the former results from the condensation of the i-plane portions of the amphiphile molecules and the latter from the condensation, at a much higher surface density, of the out-of-plane portions of the amphiphile molecules.

Cai and Rice⁵⁸ have developed a density functional theory of the tilting transition in monolayers of long chain amphiphile molecules. Their results predict both the direction and the magnitude of the tilt correctly as well as providing hints as to the origin and characteristics of the island structures that are observed when these monolayers are expanded.

B. POLYMER SURFACES

Freed and co-workers have been pioneers in developing a systematic method for calculating corrections⁵⁶⁻⁶⁵ to Flory-Huggins theory within the lattice model framework employed by Flory, Huggins, and others and also used to describe amphiphiles and polymers at interfaces. The theory for bulk phenomena begins from a formally exact integral representation of the partition function for

polymer melts, blends, or concentrated solutions, and an expansion is made in inverse powers of the lattice coordination number (z) and in powers of the van der Waals interaction energy (relative to the thermal energy). Comparisons of lattice computations of packing entropies of flexible polymers⁶¹ with Monte Carlo simulations⁶⁵ of the *identical* model show excellent agreement. Recent work extends this agreement to the energies of mixing of polymer-solvent systems.⁶⁴ Both these comparisons support the theoretical method used to discern the predictions of the lattice mode.

Recent theoretical advances enable lattice computations to be performed in which the monomers may cover several lattice sites,⁶⁰ thereby removing one of the main deficiencies of prior lattice theories, all of which require monomers, solvent molecules, and voids to occupy identical single lattice sites. The influence of the monomer size and shape dependence emerges only in the corrections to Flory-Huggins theory,⁶⁰ and a recent application of the theory to the entropy of mixing of blends⁶² shows that the entropy of mixing is dominated by the Flory-Huggins combinatorial entropy when the monomers on the two chains have the same architecture (size and shape). However, blends of polymers with different architectures have a substantial additional entropy of mixing that depends on the monomer structures.⁶⁴ This new development provides the first molecule based theory of the entropic χ parameter of Flory-Huggins theory.

D. POLYMERS AT INTERFACES

In considering the interaction of polymers with interfaces there are several relevant variables, such as the molecular weight of the polymer, the solvent quality (measuring the effective solvent mediated polymer-polymer interactions), the temperature and the polymer-interface interactions. Experiments commonly involve systematic variation of parameters such as the molecular weight, temperature and concentration, making the effective polymer-polymer and polymer-surface interaction parameters change in a complicated, concerted fashion. A goal of Freed's research^{66,67} in this area has been to provide a comprehensive quantitative theoretical description of the properties of polymers at interfaces and in confined regions using the powerful chain space renormalization group methods for polymer-surface interactions that he and his co-workers have developed. Many aspects of the single chain theory have been solved apart from those associated with strong adsorption or strong confinement. The particular projects chosen for MRL support are those which have a bearing on Rice's experiments on the structure of polymers adsorbed at liquid-vapor interfaces and the resultant modifications of the substrate structure induced by the presence of the polymers. Freed has helped to train one of Rice's students who subsequently worked on explaining⁶⁸ Rice's experiments and Monte Carlo simulations.

Often, polymers are modified so as to adsorb to surfaces by one end of the chain only; these are called grafted polymers. Grafted polymers are used to produce stable solid-liquid composites containing colloidal particles. The hydrocarbon surfactant tails in the

monolayers studied by Rice are in a similar grafted state. In such systems, the chains are grafted densely enough that they force one another into an elongated state.^{69,70} The elastic polymer stress thus generated is the source of the stabilizing force for the colloidal particles. It is also the a major factor governing the mechanical properties of surfactant membranes and monolayers.⁷¹ Witten, and Marko, together with Cates and Milner⁷² have recently developed a systematic theory, which extends and confirms earlier scaling work.⁶⁹ The new predictions of the theory have been strongly confirmed by experiments⁷³ and simulations.⁷⁴ This theory describes in a unified way both grafted chains in a solvent and copolymer chains in the strongly phase-separated limit, as discussed in Section 1A of Thrust II. It lays the groundwork for further studies proposed there, relevant to polymers at interfaces and to surfactant monolayers.

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THRUST AREA II. DISORDERED MATERIALS

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Disordered Materials Organization

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- I. Lower Dimensional Disorder: Mesoscopic and Layered Materials
(Freed, Fritzsche, Oxtoby, Witten)
- II. Glassiness and Glassy Dynamics
(Fritzsche, Halsey, Levin, Levi-Setti, Mazenko, Nagel, Rosenbaum)
- III. Order-Disorder and Structure
(Burdett, Fritzsche, Heinz, Kleppa, Levin, Levi-Setti, Newton, Rosenbaum)

INTRODUCTION:

The University of Chicago has a long and distinguished history in the study of disordered materials. In the 1930's, W. Zachariasen pioneered the analysis of the structure of glasses with his random network model for SiO_2 . In the 1960's, M. H. Cohen, in collaboration with D. Turnbull, formulated some of the basic ideas for the free volume approach to the glass transition. During the same period, Cohen and Fritzsche proposed one of the early models for the electronic properties of amorphous semiconductors. This "CFO-Mott" model has played a central role in the thinking about these materials. The experiments by Fritzsche on transport in doped semiconductors were crucial for the development of our understanding of the metal-insulator transition. In the 1970's, S. Solin studied the vibrational spectra of amorphous solids, J. Hertz developed the first gauge theory for glasses, and P. Horn did his work on the temperature dependence of $1/f$ - noise in disordered wires.

These are just a few of the many highlights that have occurred in our studies of disorder over several decades. The work we have undertaken in the last few years is no less vigorous. The activity in this thrust has been on many different fronts yet motivated by common themes. Fritzsche, Halsey, Levin, Levi-Setti, Mazenko, Nagel, and Rosenbaum have been interested in studying, by one technique or another, the generic properties of the ground state of the glass and spin glass phase. They have paid special attention to the similarities and differences between these two systems. A collaborative graduate level course given by Nagel and Rosenbaum in the Physics

Department last Spring was designed to address just this question: how much of what we know about these two systems can be related to one another.

Much of the work that has been done emphasizes prototypes which are simple enough to be understood microscopically in detail, yet complicated enough to exhibit the rich, macroscopic phenomena observed in generic glasses. A classic example of this is the collaborative Josephson-junction array work (Halsey, Levi-Setti, Nagel and Rosenbaum), in which glassy behavior was predicted to come from the uniform frustration of an applied magnetic field rather than from random impurities quenched into the system. The work by Rosenbaum and Nagel on the susceptibilities of $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ and $(\text{KBr})_{1-x}(\text{KCN})_x$ likewise was motivated by the fact that these are very simple systems where the form of the microscopic Hamiltonian is completely understood. In the former case the spins interact via dipole coupling, but the anisotropy, long range nature of the interaction, and the disorder introduced by random dilution of the Ho spins give rise to a very rich set of glassy phenomena. This study, together with the work on the Josephson-junction arrays, should allow a deconvolution of the effects of randomness from those of frustration in spin glassy systems. The orientationally disordered crystal $(\text{KBr})_{1-x}(\text{KCN})_x$, which also has a Hamiltonian that can be understood on a microscopic level, has identical low temperature thermal behavior to what is found in glasses. The susceptibility of this system was studied in an effort to see if these properties could be explained from first principles. This was truly an inter-MRL project since it relied heavily on the contemporaneous work by

members of the Cornell University Materials Science Center (J. P. Sethna and R. O. Pohl) and by the University of Illinois Materials Research Laboratory (A. C. Anderson). Levin and Mazenko have undertaken to investigate the spin glass phase, as studied experimentally by Rosenbaum. They use Monte-Carlo and other numerical techniques with simplified interactions. They have aimed to see the extent to which the complicated behavior observed in experiments on real systems can be understood in terms of simplified models. Fritzsche's research on hydrogenated amorphous silicon is not only focused on a material of considerable technological importance, but also allows the possibility of varying the dimensionality in the study of metastability and glassy dynamics in amorphous superlattices.

Considerable effort has also been spent on studying the frequency dependence of glassy relaxation phenomena. Nagel and Rosenbaum work closely together to develop techniques and models for examining and understanding their dynamic susceptibility measurements. The work on $(\text{KBr})_{1-x}(\text{KCN})_x$ and $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ has gone on in parallel with a joint MRL research associate and MRL equipment.

The work in the last section of this thrust under the title "Order, Disorder, Structure" has likewise been a well integrated program with various faculty members (Burdett, Heinz, Kleppa, and Newton) which has aimed to relate the macroscopic and microscopic phenomena of inorganic solids. The emphasis has been on understanding the order-disorder transitions of high temperature--high pressure phases of oxide systems. This project, although ostensibly distinct in the past,

has become absolutely central to one of the major new activities of our present MRL. With the advent of the new high temperature oxide ceramic superconductors, where disorder plays a profound role, the work that our MRL has been doing in the past becomes very relevant to understanding these exciting materials. Members of the project on oxides have currently joined forces with other members of this Thrust, whose expertise is in superconductivity and quantum effects (including localization) in the context of glassy behavior, to attack the crucial question of how disorder affects the properties of the new high T_c materials. Thus the various strains that have been supported in this Thrust: Josephson-junctions (Halsey, Levi-Setti, Nagel, and Rosenbaum), magnetism in disordered systems (Levin, Mazenko, and Rosenbaum), analytic ion microscopy (Levi-Setti), order-disorder-structure in oxides (Burdett, Heinz Kleppa, Newton, and Smith) and the metal-insulator transition (Fritzsche and Rosenbaum) are all coming together with their different viewpoints to focus on these new materials. We are, in fact, very proud that our MRL has been able to keep these seemingly different interests coordinated so that they could, when the opportunity arose, work together on one important problem.

There are a number of projects that are included in other Thrust Areas which are germane to the work described here. A number of studies of disordered surfaces which are described in Thrust I draw on the expertise of the Disordered Materials Thrust. Furthermore, the work on the glass transition by Freed, Mazenko, Nagel and Oxtoby, which is described in detail in Thrust III under

Dynamics of Solidification, could equally well have been included in the present thrust.

The Thrust on Disordered Materials is thus made up of three Projects which are interconnected in many ways. There are common problems approached from many different directions by researchers with different perspectives. The MRL program unites these different approaches and utilizes the different talents of our faculty to attack these problems with a common objective.

I. LOWER DIMENSIONAL DISORDER: MESOSCOPIC AND LAYERED MATERIALS

Overview: An increasing number of high technology materials involve systems with layered ordering but with amorphous structure inside the layer, or systems in which there are large scale structures randomly distributed. A characterization of the properties of these materials requires a simultaneous understanding of the microscopic behavior of the interfaces as well as of the influence of the semi-macroscopic order. Several MRL projects are designed to advance our knowledge of such systems. Witten, Oxtoby, Freed, and Olvera de la Cruz (Northwestern MRL) are studying microphase separation in block copolymer systems, where the scale and type of disorder can be manipulated through the appropriate choice of chemical constituents. Oxtoby and Freed are considering the theory of phase transitions in liquid crystals and gels, with an emphasis on understanding the combination of interactions and geometrical constraints which lead to order in some spatial directions and disorder in others. Similarly, Fritzsche manipulates order and

disorder through his continuing investigations of amorphous semiconductor superlattices. Here, the effects of disorder in two dimensions can be modulated by the imposition of order, or even quasiperiodic order, in the third dimension.

A. MICROPHASE SEPARATION IN BLOCK COPOLYMERS

When a diblock copolymer undergoes phase separation, the two components cannot separate fully from one another because they are chemically bonded. Consequently, there only can be microphase separation, which produces a number of morphologies: lamellae, cylinders, and close packed lattices of one component surrounded by another. The observed phase diagrams depend on the nature of the two components and on the relative proportions of the two in the block copolymer. Composites made from these materials have properties that are strongly influenced by the phases from which they are fabricated. Witten, Oxtoby, and Freed are developing a new theory of microphase separation in collaboration with Monica Olvera de la Cruz (Materials Science and MRL, Northwestern University).

Olvera has developed a theory of the phase separation of block copolymers,¹ but the theory is restricted to the prediction of the coexistence curve between the melt and the ordered phase, and it does not describe the structure of the ordered phase. Other theories of microphase structure^{2,3} only contain a single wavevector to describe the ordered phase.⁴ Their use of a Landau expansion of the free energy density with only one order parameter (i.e., one wavevector) is correct only if the transition is very close to second order. Such approaches, when applied to the freezing of simple

molecules, incorrectly predict the appearance of a body centered cubic rather than a face centered cubic lattice,⁴ and they cannot account for the first order behavior of the observed transition. Recent work by Fredrickson and Helfand⁵ implies that the microphase separation in block copolymers can never be second order, thus undermining a primary assumption of much of the prior work and emphasizing the need for the development of a new theory of the structure of the microphases that is based on a theory of freezing with the following characteristics: (a) It must be applicable to first order phase transitions; (b) It must correctly predict the observed freezing to a face centered cubic solid for simple molecules; (c) It must be capable of distinguishing between various possible microphase structures. Such a theory is provided by Oxtoby's theory of freezing.

Oxtoby has been one of the pioneers in applying modern density functional techniques to the description of the freezing of simple liquids where the theory correctly predicts the emergence of a face centered cubic phase.⁶⁻¹¹ He has shown how the theory of nonuniform liquids can be used to predict both equilibrium and time-dependent properties of the freezing transition. One of the powerful features of this method is that it uses input information about correlations in the disordered phase (liquid) to predict the properties of the resulting ordered phase. This information can be obtained theoretically, or it can be obtained from experimental measurements of the structure factor (from neutron or light scattering) of the disordered phase. As a result, the theory is

applicable even to rather complex systems for which full a priori calculations would be impossible.

Having undergone a phase separation like that discussed above, block copolymers may reach a *strongly* phase separated state, in which the microdomains are indefinitely larger than the interface between the two types of blocks. In this strongly phase-separated regime the stretching of the chains is important. The stretching energy and the interfacial energy combine to control the equilibrium domain morphology and size.¹² To treat the domains quantitatively it is necessary to find a self-consistent ensemble of polymers in the layer which satisfies both the constitutive condition of nearly uniform density and the equilibrium of forces along the chains.¹³ Recently¹⁴ our understanding of the grafted state has been improved by a systematic analytical theory by Witten, Marko, Cates and Milner.¹⁵ The new theory is strongly confirmed by simulations¹⁶ and experiment.¹⁷

The diblock copolymers described above often make disordered layers which appear in cross-section or in thin-film samples as disordered stripes.¹⁸ Similar patterns also occur in ferrofluid/normal-fluid mixtures in a magnetic field¹⁹ and in magnetic-bubble material being studied in Libchaber's lab.

B. PHASE TRANSITIONS IN LIQUID CRYSTALS AND GELATION

Oxtoby's earlier work shows how the simplest implementation of the density functional approach for molecular liquids leads to a generalization of the McMillan theory of the isotropic-nematic-

smectic phase diagrams. Generalized models are possible that provide more realistic descriptions.²⁰ It has been known for some time that polymers such as polyethylene crystallize into platelike structures,²¹ and considerable progress has been made in the description of the dynamics of this transition.²² However, only lattice models have been used and these cannot describe the molecular behavior on a microscopic scale, nor can they predict the parameters that should go into the lattice models. The recent work of Chandler et al.,²³ showing how to incorporate bond constraints in a density functional theory, should be very helpful in this regard, and Freed's lattice theory²⁴⁻³⁰ may be useful for introducing more realistic interaction parameters.

Some aspects of the co-operative metastability seen in glasses occur in associating polymer solutions. Associating polymers are flexible polymer chains with a small fraction of monomers modified so as to be strongly immiscible with the others. These monomers act as "stickers", which combine reversibly into small "multiplets". These multiplets link the chains in the solution to themselves and to one another. The networks thus formed are labile; the multiplet crosslinks may have lifetimes on the order of seconds. The networks are apparently strongly sensitive to flow, since mild shear flow can induce dramatic, reversible gelation phenomena.

Murat and Witten³¹ have recently devised a new Monte-Carlo algorithm for studying the statistics of such labile networks.

C. AMORPHOUS SEMICONDUCTOR SUPERLATTICES

The study of quantum size effects in ultrathin multilayers consisting of amorphous semiconductors and insulators offers a direct measurement of the characteristic length scale of the wavefunctions of extended and localized states. These quantities cannot be calculated and are not easily deduced from other experiments because of the lack of translational symmetry in amorphous materials. In agreement with other workers,³² Fritzsche's group observed³³ an increase in the optical gap of hydrogenated amorphous silicon as layers of this material sandwiched between insulating silicon nitride are made thinner than 60 Å. Doubt was expressed³⁴ that this effect is caused by quantum confinement of electrons and holes in the less than 60 Å thin films of semiconductors. The doubts were based on possible alloying of the silicon layers with nitride and on the surprise that the coherence of the extended state wavefunctions survived over such a distance.

In order to resolve the controversy, Fritzsche compared time resolved photoluminescence of simple amorphous silicon layers with single silicon nitride layers, and with multilayers made of the two materials, and showed that quantum confinement effects are indeed observed when the silicon sublayers are less than 60 Å thick.³⁵ This conclusion agrees with the finding that the interfaces are sharply defined to a width of two atomic layers.³⁶

Given the atomically sharp nature of the superlattices, it is possible to impose periodic order on the atomic length scale. Recent resonant tunneling and modulation experiments have given clear proof of the one-dimensional quantization of the conduction and valence band states in ultrathin superlattices.³⁷ The quantum states can be fitted using a Kronig-Penny model, with an electron effective mass of $0.3 m_e$. The expected selection rule $\Delta n = 0$ for optical transitions between the quantized levels in the valence and the conductance band are obeyed, indicating good phase coherence.

II. GLASSINESS AND GLASSY DYNAMICS

Overview: One of the hallmarks of the MRL research in glassy or disordered systems is finding a simple prototype which has many or all of the features of "canonical" glasses and yet is easy to characterize microscopically. Nagel's work on the elastic glass, $(\text{KBr})_{1-x}(\text{KCN})_x$, has been the leading effort in understanding the microscopic origin of two-level-systems and in establishing their quantitative contribution to the specific heat and glassy relaxation. Rosenbaum's complementary studies of the model dilute dipolar-coupled Ising magnet, $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$, has opened the possibility of studying the interplay and relative importance of disorder and frustration in spin glasses. Fritzsche's research on hydrogenated amorphous silicon opens new possibilities for investigating glasses without crystal antecedents and offers the additional variable of altering dimensionality in his study of metastability and glassy dynamics in amorphous semiconductor superlattices. In addition, his discovery of low temperature universal behavior in amorphous

semiconductors promises a route to connecting the glassy behavior of a diverse range of materials. The theoretical analysis is provided in part by Levin and Mazenko, who have focused their efforts on magnetic glasses such as spin glasses and random field systems with the general philosophy that these represent microscopically well-defined glassy systems which lend themselves to a direct theoretical treatment.

A. ELASTIC AND MAGNETIC GLASSES

The low temperature properties of glasses are not yet fully understood largely because of the complicated structure of these materials. The discovery that certain crystals, such as the cubic crystal $(\text{KBr})_{1-x}(\text{KCN})_x$, behave in ways characteristic of glasses thus presents an opportunity to construct a microscopic model of glassy dynamics.

A number of experimental probes have indicated that $(\text{KBr})_{1-x}(\text{KCN})_x$ has glass-like behavior over a wide composition range. For $T < 10$ K, the thermal properties^{38,39} are the same as in glasses. There is a specific heat, C_p , approximately linear in T , and a thermal conductivity which varies as T^2 . At high temperature, $(\text{KBr})_{1-x}(\text{KCN})_x$ undergoes a transition much like an actual glass transition, as has been seen in ultrasonic,⁴⁰⁻⁴² shear modulus,⁴³ Brillouin⁴⁴ and inelastic neutron^{40,45,46} scattering experiments. One also sees behavior^{43,48,48} at intermediate temperatures analogous to β -relaxation in glasses.

Nagel and his students have studied this β -relaxation as it appears in the dielectric response of $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ over a wide

Nagel and his students have studied this β -relaxation as it appears in the dielectric response of $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ over a wide range of frequency and temperature.⁴⁸ They saw a very wide peak in the dielectric loss function, ϵ_2 , which is indicative of relaxation phenomena. In order to study the relaxation in detail, they measured the susceptibility over 9 decades in frequency using a variety of techniques and were able to show that the peak in ϵ_2 moved in an Arrhenius manner with temperature. The shape of the peak was Gaussian (in log frequency) and increased in width as the temperature was lowered. In particular, they were able to express the dielectric response as due to a distribution of relaxation times which were, in turn, derived from a Gaussian distribution of energy barriers. The width of this distribution of energy barriers also increased as the temperature decreased.

The two-level system model of Anderson, Halperin and Varma⁴⁹ and Phillips⁵⁰ assumes that throughout the glass there are two-level systems which arise from the tunneling of some structural entity between two nearly degenerate states. However, little is known as to what these entities actually are. Because of its simple lattice structure, one can construct from first principles a microscopic model of the glassy dynamics in $(\text{KBr})_{1-x}(\text{KCN})_x$. Such a theory, developed by Sethna et al.,⁵¹ maintains that the same process is responsible for both the glassy low T thermal properties and the high T dielectric response studied by Nagel. At a high temperature, T_q , the dipole axis of each CN molecule is frozen into a random orientation (i.e., there is a quadrupolar transition). Below T_q , the CN molecules can still flip by 180° . Because there is an electric dipole

moment, this motion of the CN appears in the dielectric response as a relaxation peak. The low temperature behavior is presumed also to be caused by the 180° flips of the CN, but instead of thermal activation over the barrier, responsible for the dielectric behavior, tunneling through the activation barriers is the dominant process. The theory uses as a starting point the distribution of activation energies derived from Nagel's dielectric measurements.⁴⁸ With a few additional plausible assumptions about $(\text{KBr})_{1-x}(\text{KCN})_x$, this model predicts a low T specific heat in good agreement with the magnitude and time dependence seen in experiments.

In order to test Sethna's theory in greater detail, Nagel and his students have made a careful study of the dielectric response of the $(\text{KBr})_{1-x}(\text{KCN})_x$ system as a function of concentration, x . This has allowed them to check the predictions of the theory and compare with the low temperature specific heat data obtained by the Cornell group.³⁸ They have found^{52,53} that the dielectric response can be well fit by a log-normal distribution of relaxation times for all alloy compositions.

The width of the activation energy distribution increases as temperature is lowered for each composition, just as occurred for $x = 0.50$. Using the parameters that were used to fit the $x = 0.50$ data, they were then able to calculate the number of tunneling levels that would contribute to the low temperature specific heat. This number depends critically on the position and width of the activation energy distribution for each composition. They found excellent agreement (within 10%) between the number calculated from the dielectric response and the number actually observed in the specific heat

experiments.³⁸ Also a comparison was made of the time-dependent specific heat data and the prediction from the dielectric data using the Sethna model. Again the agreement is quite convincing. This is an important confirmation of the Sethna model which may indicate that it is more generally applicable to real structural glasses.

We also note that the dielectric data as a function of composition has helped confirm the mean field theory of the quadrupolar freezing which was worked out by Sethna, Nagel, and Ramakrishnan.⁵⁴ In particular, the linear T dependence of the order parameter at low temperatures predicted by the theory was found to be necessary to explain the newest set of measurements.

$(\text{KBr})_{1-x}(\text{KCN})_x$ is a simple system which can be characterized in detail, yet its behavior is sufficiently complicated to be interesting and in fact, a useful paradigm for structural glasses. With similar intent, Rosenbaum and his group have been studying the dilute, insulating, dipolar-coupled Ising magnet $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$. Here, Ising dipoles occupy randomly chosen sites of a regular lattice. The microscopic Hamiltonian is completely understood, but the anisotropy and long-range nature of the dipolar interaction, combined with the disorder introduced by replacing the magnetic Ho^{3+} ions with non-magnetic Y^{3+} , provide for a rich spectrum of physical responses. In particular, different regimes of magnetic glassiness can be accessed by varying the holmium concentration x . A comparison of the dynamic response in the separate glassy regions allows the possibility of deconvoluting the effects of randomness and frustration in spin glasses.

Rosenbaum's group has measured^{55,56,57} the a.c. magnetic

susceptibility for variously diluted samples over six decades of frequency, in analogy to Nagel's approach to $(\text{KBr})_{1-x}(\text{KCN})_x$, and for temperatures between 10 mK and 1K. For x larger than, at most, 0.46, the members of the isostructural $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ series order ferromagnetically at $T_c = xT_c(x=1)$, with $T_c = 1.53$ K for pure LiHoF_4 . On the other hand, for $x < 0.17$, no evidence for ferromagnetic order above $T = 10$ mK has been found, even when samples are cooled in magnetic fields up to $H = 80$ kOe.⁵⁵

The temperature evolution of the imaginary parts of the a.c. susceptibility for the two most dilute samples, $x = 0.045$ and $x = 0.167$, have been compared where the magnetic response at different temperatures is scaled by both peak frequency and peak height.^{56,57} In both cases, the full width at half maximum is broader than the Debye form (1.14 decades in frequency); the response cannot be described by a single relaxation time τ . The more concentrated sample, however, has a considerably wider distribution of relaxation times, and it broadens symmetrically with temperature, while the very dilute sample only broadens at low frequency. But most importantly, the $x = 0.045$ sample has an enhanced low frequency response at *high* temperature while the $x = 0.167$ sample follows more conventional spin glass behavior⁵⁸ with an enhanced low frequency response at *low* temperature. These contrary responses correspond to a progressive loss/gain of high barriers to spin relaxation, respectively, as temperature is reduced. Thus, $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ is a model system which should enable the study of the evolution from a simple glass, whose dynamics are dominated by activation over fixed barriers, to a more correlated state of the type commonly associated

with spin glasses, or the random field problem studied by Levin and Mazenko.

One of the main goals of Levin's spin glass research has been to understand the origin of irreversibility and metastability in these systems. Similar behavior and a similar type of approach has been taken for the random field Ising systems. In both of these classes of materials one sees profoundly history dependent behavior.⁵⁹ This is most clearly evident by comparing field-cooled and zero-field-cooled measurements of thermodynamic properties and, in particular, the magnetization. At some "critical value" of the magnetic field, H , for a given temperature, the experimentally observed magnetizations are no longer equivalent; the discrepancy between the two different magnetizations grows with decreasing field and decreasing temperature. In the random field systems (such as $\text{Fe}_x\text{Mn}_{1-x}\text{F}_2$) antiferromagnetic long range order is accessed only when the system is cooled in zero magnetic field. In the field cooled configuration the material breaks up into magnetic domains.

The theoretical approach Levin has adopted to understand this irreversibility is based on studying the evolution of the free energy surface as H and T are varied in a manner prescribed by the experimental situation.⁶⁰ The underlying hypothesis is that at sufficiently high temperatures, or at sufficiently high fields, there is a single minimum of the free energy surface. As T or H decreases, more and more minima are created. On a short time scale, the glassy system will move from one minimum to another only if the minimum in which it originally resided has disappeared. This will happen upon heating or upon increasing H . Then the system

reequilibrates and falls into the closest near-by state. On short time scales the complex topology of the free energy surface completely determines the irreversible behavior.

How does one characterize in a precise way the topology of the free energy surface? This is a key question which relates not only to short time irreversibility, such as discussed above, but also to the longer time relaxation processes which are generally associated with "glassy dynamics," and the measurements of Fritzsche, Nagel, and Rosenbaum. Monte Carlo simulations yield some insight into this issue, but they do not directly provide one with a "picture" of the free energy surface. Rather, they generate in some sense more "experimental" data in a theoretically well-characterized system. As a complementary approach, Levin's group has been studying⁶¹ the free energy surface of mean field models of spin glasses and random field systems. The shortcomings of mean field approaches are well known. Nevertheless, they are amenable to numerical treatment for systems containing of the order of several million spins. It was recognized some time ago that these mean field simulations reproduce all the qualitative features of the data: hysteresis loops, magnetic remanences, etc., all bear striking resemblances to their experimental counterparts. In brief, the mean field simulation consists of solving the mean field equations iteratively under variations in field and temperature which coincide with field-cooled, zero-field-cooled, or other experimentally prescribed configurations. In this way, a system will follow a given minimum until it disappears, and then find its way to a near-by state. This scheme thus simulates the physical picture of short time irreversibility,

discussed above.

A general theme in the MRL research on glassy systems is a characterization of the glassy dynamics. In an effort to make contact with this area of collective interest, and to assess more fully the utility of numerical mean field approaches, Levin's group was led to follow Monte Carlo simulations as a function of (Monte Carlo) time side by side with the mean field simulations. By using the same starting distribution of exchange interactions, one could make direct comparisons. This was done in considerable detail for the random field Ising systems.⁶² As was anticipated, the longer the Monte Carlo simulation was allowed to run, the greater the deviation from the mean field results. In fact, for sufficiently long runs, the simulations yielded thermodynamic equilibrium and, hence, reversible behavior. Since true equilibrium is difficult, if not impossible to obtain experimentally in these glassy magnets, long time Monte Carlo simulations did not match laboratory behavior. Nevertheless, these studies are valuable because they allow one to watch the system access larger and larger regions of phase space, and thereby wash out the signatures of glassiness.

The work of Mazenko on growth kinetics (see Thrust I) also bears on the studies of elastic and magnetic glasses described here. In the course of the development of a renormalization group theory for growth kinetics problems, Lai, Mazenko and Valls⁶³ have shown that systems with quenched impurities (e.g., the random field Ising model, dilute ferromagnets, etc.) belong to different growth kinetic "fixed points" than pure systems. These random fixed points are associated with logarithmic time behavior and relaxation processes,

while pure systems show power law growth with time. Rosenbaum and his group recently have made preliminary neutron scattering measurements⁶⁴ of $\text{LiH}_{0.167}\text{Y}_{0.833}\text{F}_4$, in an attempt to understand the local cluster dynamics, with possible connections to Mazenko's work on quenched systems.

B. GLASSINESS AND METASTABILITY IN HYDROGENATED AMORPHOUS SILICON

A most important and startling recent discovery was the finding that bonded hydrogen in hydrogenated amorphous silicon (a-Si:H) forms a subsystem with all the characteristic properties of a glass.⁶⁵ The diffusing hydrogen⁶⁶ mediates the equilibration of the short-range bonding configurations that govern the concentrations of dopants and of defects above the glass transition temperature of $T_g \cong 130^\circ\text{C}$. Equilibrium occurs progressively slower as T is lowered below T_g , and equilibrium conditions above T_g can be frozen and studied at low temperatures by rapid quenching. The equilibrium concentrations of donors and dangling bond defects above T_g depend on the position of the Fermi level⁶⁷ and, hence, should be changed by strong light exposure. Fritzsche found and studied this effect⁶⁸ by equilibrating a-Si:H above T_g under strong illumination instead of darkness and preserving this new state by quenching to room temperature. The metastable changes in donor and defect concentrations required much longer time and higher activation energies for annealing when produced with illumination than without. Moreover, in contrast to others, they found⁶⁹ that the equilibrium concentrations of both donors and defects increased with

temperature above T_g .

Lower dimensional samples additionally provide the opportunity for the study of glassy dynamics. Fritzsche and his students have studied the creation of metastable nonequilibrium states both in single layer films of a-Si:H and in multilayers that either consist of several hundred Angstroms thick alternating layers of n-type and p-type a-Si:H or of tens of Angstroms thick alternating layers of a-Si:H and insulating silicon nitride. In single layers they observed two effects: (i) the energy and configurational environment of photo-created metastable defects depends on the temperature of light exposure between 4.2 and 400 K,^{70,71} and (ii) the equilibrium of the defect and dopant concentrations above the equilibrium temperature, $T_e = 150^\circ\text{C}$, depends on the Fermi energy, E_F . These concentrations can be altered by changing E_F either by strong illumination⁷² or by space charge injection. This is related to the fact that the defects and dopants are oppositely charged and that their creation energy depends on E_F .

Fritzsche and coworkers reinvestigated the effect of mechanical stress on the photo-induced creation of metastable defects in a-Si:H. Since stress weakens some Si-Si bonds, more bonds should be susceptible to breaking during electron-hole recombination. In contrast to an earlier report,⁷³ they did not observe such an effect.⁷⁴

Using the traveling-wave method they studied as well the effect of light-induced metastable defects on the electron drift mobility in a-Si:H. They observed an appreciable decrease of the drift mobility with increasing concentration of dangling bond defects.⁷⁵ However, in contrast to observations of an increase in drift mobility with double injection of electrons and holes, they failed to see such an increase

when excess electron-hole pairs were excited by light.

Fritzsche observed metastable excess conductance states both in multilayers in which thin a-Si:H layers are sandwiched between insulating nitride and in doping-modulated multilayers. In the former, these metastable states result from self-induced space-charge accumulations across the silicon nitride insulators. They can be removed by a discharging light pulse.^{76,77} In the latter, he found a photo-induced excess conductance, called persistent photoconductivity (PPC)^{78,79} as well as new metastable states that are produced by cooling the doping-modulated multilayers while a bias is applied.^{80,81}

The long time constants of the order of days and weeks at 24 °C, and the large anneal activation energies ($\cong 1.2$ eV) of these metastable states, suggest as their origin changes in bonding configurations of dopants or host atoms. It is likely that diffusing hydrogen plays a major role, yet the detailed interactions remain unclear.

Finally, Fritzsche's group has discovered universal trends in the electron transport and photo-carrier recombination in disordered semiconductors. A common feature of disordered materials are tails of localized states at both the top and bottom of the bands of electron eigenstates. These localized tail states depend on the disorder potential of a given material.⁸² Since conduction in semiconductors takes place near the band edges, these localized tail states affect in a crucial manner the electronic properties of disordered semiconductors. Fritzsche et al. have derived universal expressions for the recombination of photo-excited electron-hole pairs and their

diffusive hopping motion in amorphous semiconductors at low temperatures.⁸³⁻⁸⁵ At low temperatures only energy-loss hopping is possible. The problem of the competition of energy-loss hopping to a nearest-neighbor localized state and of recombination can be reduced to a general mathematical problem involving only random sites in three dimensions. They find that the solution is independent of the energy dependence of the density of localized states and hence independent of the semiconductor material.⁸³⁻⁸⁵ The theory predicts that the photoconductivity at low temperatures is of the same order of magnitude in all amorphous semiconductors. They have measured seven different materials and indeed have found this to be true.^{86,87}

III. ORDER-DISORDER AND STRUCTURE

A. OXIDES

The collaboration of Newton and Kleppa combines phase equilibrium measurements and high-temperature solution calorimetry to measure, respectively, free energy and enthalpy in systems of refractory oxides. This combination of complementary disciplines at one institution is still practically unique: a high-temperature solution calorimetry facility is under construction at Cambridge University, where high-temperature, high-pressure experimental apparatus exists, but ultimate development of a joint facility of the same capability as the one at Chicago is still some distance in the future.

One major effort in the past two years has been to clarify the energetics of solid solution in ternary garnets of the formula $(\text{Ca}, \text{Fe}^{2+}, \text{Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12}$. These substances are technologically important as well as being natural minerals. Substitution on the large eight-coordinated X-site of garnet has many interesting theoretical aspects, among which is analogy to the eight-fold divalent cation site of the perovskite structure. The eight-coordinated site in garnet is well-suited in size to Ca but somewhat too small for Fe^{2+} and Mg; from this circumstance arise the possibilities of site-distortion, with repercussions for crystal-field splitting of Fe^{2+} , especially in solid solutions with Ca, of clustering of cations analogous to that demonstrated for Ca, Mg carbonates,⁸⁸ of very anisotropic thermal vibrations, which lead to entropy stabilization, as we have demonstrated in previous work for the Mg garnet (pyrope: ^{89,90}), and positional cation disorder within the X-site.⁹¹

Previous calorimetric work at Chicago has demonstrated the near-ideality of cation substitution along the Ca- Fe^{2+} join, the small asymmetric non-ideality along the Fe^{2+} -Mg join, and the large asymmetric non-ideality along the Ca-Mg join.^{92,93} We have recently confirmed the ideality of the Ca- Fe^{2+} join by phase equilibrium measurements involving precise measurements of the pressure threshold of breakdown of anorthite feldspar to Ca (grossular) garnet and the effects of Fe^{2+} (almandine) substitution thereupon.⁹⁴ The Calorimetric prediction of (Ca, Mg) substitutional non ideality was strikingly confirmed last year by independent phase equilibrium measurements.⁹⁵ This study also

confirmed our low-temperature heat capacity findings of excess entropy on the join as a stabilizing factor.⁹⁶

One type of phase equilibrium measurement which Newton and Kleppa have used effectively to define solid solution energetics is experimental cation partitioning between coexisting phases. An extensive study of Fe^{2+} , Mg partitioning between coexisting garnet and clinopyroxene ($\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$) has recently been completed. In the diopside-hedenbergite solid solution, the Mg and Fe^{2+} are ordered on the smaller and more irregular M1 octahedral site. Previous attempts^{97,98} at phase-equilibrium definition of the free energy of this solid solution have concluded that the join is characterized by symmetric excess free energy. Our Fe^{2+} , Mg distribution isotherms⁹⁹ reveal an asymmetric non-ideal with considerably more detail, however. The non-ideality in clinopyroxene is nearly independent of the free energy of substitution in pyrope-almandine garnets--which we have shown to have modest non-ideality.

Burdett, Heinz, and Newton are jointly studying this fascinating ability of Fe^{2+} to stabilize garnet solid solutions, as a part of a more general study of the area of the energetics of solid solutions in oxides. Burdett's theoretical study centers around the modelling of the ordering pattern of the metal atoms in the structure and the thermochemical gain associated with certain arrangements. The calculations are of the tight-binding type with overlap. Using a large unit cell the energy of all $\text{A}_x\text{B}_y\text{O}_{x+y}$ permutations ($x + y = \text{const.}$) is calculated. The permutationally averaged energy for a given stoichiometry, combined with the

energies of the two end-members ($x = 0$ and $y = 0$) is used to compute ΔH_{xs} curve. The results¹⁰⁰ are extremely interesting. Starting with the simple rocksalt structure for which there is quite a bit of experimental data, ΔH_{xs} curves for both the MgO/FeO and MgO/NiO systems have been calculated which readily reproduce the difference in sign found experimentally for these two systems. This is quite a significant result. Considerable progress has been made in the dissection of the calculations to understand the nature of the factors which control the sign and magnitude of the values observed experimentally and reproduced numerically. Important parameters include the change in volume as x and y change. Progress is beginning to be made in the understanding of the electronic conditions for the observation of the 'reentrant' type of behavior observed experimentally by Newton in the garnets. A problem of related interest is associated with the rates of reaction involving the molecular redox catalyst $\text{PMo}_x\text{W}_{12-x}\text{O}_{40}^{3-}$ studied by Misono et al.¹⁰¹ Here we see a dependence of the reaction rate on the composition in a fashion reminiscent of the ΔH_{xs} curves for the oxides. In fact our calculations of the redox potential of these 'solid solutions' mimic the shape of Misono's curve.

Given that the molecular orbital which determines the redox potential, when occupied determines ΔH_{xs} , the correlation between the two apparently distinct areas of chemistry is now established. The electronic explanation of the effect in these molecular systems is certainly the same as that controlling the energetics of the solids.

Heinz has measured the equation of state of the high pressure phase of KCl (CsCl structure or B2 phase) to test the accuracy of quantum mechanical equations of state for the CsCl structure. The equation of state of the high pressure phase of KCl has been measured to 56 GPa. Previous calculations (Augmented Plane Waves, Modified Electron Gas and Pseudopotential (referenced in 110) have been shown to be very accurate for the B1 phase (zero pressure phase) of NaCl, but there appeared to be a systematic offset for the B2 phase¹⁰² or high pressure structure of NaCl for all the theoretical calculations, which only shared the local density functional for electron correlation. The interesting result of the current study is that the deviation of the predicted equation state from the measured equation of state for the B2 phase of KCl is opposite that for NaCl.¹⁰³ We are interested in the theoretical descriptions of high pressure phases, in light of the collaborations of Burdett and Heinz. It should be noted that the overall agreement of the theoretical calculations and the experiments is quite good. Our equation of state is in very good agreement with the previous measurements to approximately 10 GPa.¹⁰⁴ The value of Bulk Modulus, the pressure derivative of the bulk modulus, and the zero pressure volume of the B2 phase relative to the zero pressure volume of the B1 phase are 28.1 (6) GPa, 3.9 (2), and 0.850 (6) respectively. Both the B1 and B2 structures are the structures which occur in some of the simple monosulphides that Heinz and Burdett are studying.

Heinz has also measured the equation of state of MnS in the NaCl structure to 25 GPa, at which point it transforms to a yet-to-

be-determined structure (which we know has tetragonal or lower symmetry). The measured bulk modulus of 87 (5) GPa and its pressure derivative of 4 are in agreement with previous studies.¹⁰⁵ Several previous studies have reported a phase transition at approximately 10 GPa;^{105,106} we were unable to verify these results.

In addition to the above work, Heinz¹⁰⁷ has carried out calculations on the effect of thermal pressure in laser heated diamond anvil cell samples that are contained in solid pressure media. When the volume of a heated sample is constrained the pressure is raised due to the thermal expansion of the material. This is what happens in a laser heated diamond anvil cell when the pressure medium is a solid. The calculations have shown that the thermal pressure is quite large and will affect the locations of phase boundaries. In light of this, Heinz is developing a system to load argon, which can melt, as a pressure medium, so that thermal pressures can be distributed over the entire sample volume. This work is in preparation for using the laser heated diamond anvil cell on the synchrotron at Brookhaven to study sulfides at simultaneous high temperatures and pressures.

B. SUPERCONDUCTING OXIDES

It is clear that the properties of the high T_c superconductors are strongly controlled by their geometrical structure, and in particular the ordering patterns of the oxide ions within a metal framework. Compare this then with the ordering patterns of the metal ions over the sites of an oxide array (or a sulfide array in

Section IV) which has been an active area of research at Chicago for many years. It is related as well to the question of ordering of chemisorbed species on surfaces, addressed in another part of this proposal. This area is then one where the interests of many of our MRL members overlap. The chemical questions associated with the oxide ordering in the superconductors lead to understanding concerning the variations to be expected in the electronic band structure, of direct interest to both experimental and theoretical physicists. The expertise in this area is of direct relevance to thermochemical studies of cation ordering in the garnet and related structures. The collaboration of Burdett and Levin (theory) with Rosenbaum (experiment) in understanding the electronic, magnetic and transport properties of these system is quite analogous to that of Burdett (theory) with Heinz (experiment) in the area of sulfides.

Burdett and Levin began their collaboration¹⁰⁸ with a study of the electronic structure of oxygen defects in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$. They see important deviations from rigid band behavior and their results depend sensitively on the location of the site from which the oxygen is removed. Particularly in the 1-2-3 compound, there are many inequivalent oxygen sites so that the electronic structure reflects the local environment of a given oxygen. Burdett has recently shown how the orthorhombic-tetragonal transition is electronically driven¹⁰⁹ and has suggested that although the superconductivity mechanism may be exotic the electronic structure is quite conventional.

Levin's research has focussed on the normal state properties of the oxides and has made considerable use of the chemical insights from Burdett and his colleagues. There have also been interactions with Rosenbaum, particularly on parallel studies of heavy fermion and copper oxide superconductors and on anomalous transport properties of the cuprates.

Levin has built on her Fermi liquid picture¹¹⁰ (discussed in the previous proposal) to calculate the magnitude of the electron phonon interaction in the strongly correlated copper oxides and its effect on the temperature dependent resistivity. They used a scheme similar to the bandstructure approaches of Burdett but have also added the effects of (infinitely) strong Coulomb correlations which lead to pronounced band narrowing. Electron-phonon interactions are deduced in a "frozen phonon" scheme¹¹¹ by introducing a static distortion of the copper or oxygen atoms and calculating the resulting shift in the (Coulomb renormalized) bandstructure. Near half filling, the strong Coulomb correlations suppress charge transfer and therefore, make the electron-phonon coupling extremely weak. On the other hand, these correlation effects increase the effective mass so that the contribution to the electrical resistivity consists of two competing effects.

The electron-phonon contribution is nearly linear and its magnitude is close to that measured experimentally,¹¹² except at low doping concentrations near the insulating limit. Furthermore, using ac conductivity measurements, comparison can be made separately with the n/m^* and lifetime contributions to the resistivity. Levin and co-workers¹¹¹ find that both components

agree with their experimental counterparts^{113,114} within factors of two.

The source of the remarkably linear temperature dependent resistivity in the oxides has been the subject of much speculation and controversy. This linearity (which is sometimes observed down to very low temperatures ≈ 20 K) may not be due exclusively to an electron-phonon mechanism. On the other hand, the essential point of this work is to determine the electron-phonon "background" contribution which is clearly present in a Fermi liquid description and must be subtracted out in order to determine the presence of additional contributions which may, say, be due to electron-electron scattering.

Recently, Levin and her group have begun a systematic comparison of data in the heavy fermion metals (which are known to be Fermi liquids at sufficiently low temperatures) and the copper oxides. The purpose of this study is to determine to what extent anomalous transport and magnetic data in the cuprates are similar to their counterparts in the strongly correlated heavy Fermi liquids. This study has led to some striking insights.

The conclusion is that the temperature dependent behavior seen in the oxides reflects that of the heavy fermions in their low temperature, "coherent" regime. The deviations from linear behavior in $1/T_1$, which linearity is characteristic of a Fermi liquid, become apparent at a temperature T_{coh} which is around 150 K in the oxide and 1.5 K in the heavy fermion. Above this temperature the nearly localized d (or f) electrons begin to lose their itinerancy and the Fermi liquid becomes progressively less

coherent. Other similar comparisons with a rescaled temperature or frequency axis for the ac conductivity and for the temperature dependence of the Hall coefficient have been made. The same rescaling procedure has been used on the heavy fermion systems (corrected for the slightly different m^* in each system). These three comparisons collectively indicate that there are strong similarities, albeit on different energy scales, between the two systems. The general conclusion is that the copper oxides may, indeed, be Fermi liquids and that the "anomalous" temperature dependent behavior observed in the normal state can be attributed to the gradual break-up of coherence which occurs slightly above the superconducting transition.

Levi-Setti's ion microprobe is ideally suited for high resolution (30-40 nm) chemical mapping of the high T_c superconducting ceramics. He has concluded an ion microprobe characterization of laser-deposited $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (1-2-3) thin films,¹¹⁵ undertaken in collaboration with T. Venkatesan of Bell Communication Research and his colleagues at Rutgers University and Middlebury College. This study, which exploited the high lateral resolution (< 50 nm) of the UC ion microprobe in imaging microanalysis by secondary ion mass spectrometry, addressed the effects of anneal temperature on the structure and composition of the films. The thin films were deposited on SrTiO_3 substrates by pulsed laser evaporation of bulk stoichiometric 1-2-3 pellets derived from either BaCO_3 or Ba_3N_2 . The grain growth, film-substrate interaction, and carbon contamination of the films were examined as a function of post-deposition anneal

temperature ranging between 700° C and 900° C. On the surface of both types of film, overgrowth crystals were found, which are enriched in Cu, that increased in size from a few tenths of a micron to several microns with increasing anneal temperature. Above 800° C the films form a polycrystalline structure with grain size $\approx$ 1 micron. With increasing anneal temperature, more Sr was observed on the surface of the films. Films derived from 1-2-3 targets in turn originating from BaCo_3 and Ba_3N_2 were both contaminated with carbon; however, only the former showed segregated carbon along the grain boundaries of the polycrystalline films annealed at 900° C. These observations provided guidance to Bellcore for the fabrication of films with superior structural and transport properties.

Another collaborative study has been concluded,¹²⁸ as part of an ongoing collaboration with SIMS laboratory of A. Lodding at Chalmers University of Technology, Goteborg, Sweden. This investigation was addressed at the identification of a number of non-superconducting phases which are found in bulk 1-2-3 superconducting ceramics. A very complete chemical characterization of samples prepared at the University of Florida was performed, by quantitative high sensitivity SIMS microanalysis at Chalmers, complemented by high lateral resolution SIMS imaging at UC. Maps were obtained for many elements (O, Y, Ba, Cu, C) and compounds or clusters (O_2 , OH, C_2 , CN, BaO, CuO, YO, YO_2) and several of the phases present (2-1-1, 0-1-1, 2-1-0, as well as Y, Ba, Cu excess oxides) could be identified by correlative image processing techniques. This pilot study

established the feasibility of quantitative characterization of bulk high- T_c superconductors by SIMS techniques over the full range of domain sizes down to a few tenths of nanometers.

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THRUST AREA III: DYNAMICAL PATTERNS AND SOLIDIFICATION

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Dynamical Patterns and Solidification Organization

Coordinators: L. P. Kadanoff and G. F. Mazenko

- I. Dynamical Patterns
 (Fritzsche, Halsey, Kadanoff, Libchaber, Nagel)

- II. Dynamics of Solidification
 (Freed, Mazenko, Nagel, Oxtoby)

- III. Seed Area: Convective Turbulence
 (Kadanoff, Libchaber)

INTRODUCTION:

This Thrust is concerned with the dynamics of pattern formation and dynamical evolution under many different physical circumstances. One place where pattern formation commonly occurs is at the interface between two distinct phases. Here the instabilities of a moving front can create patterns of such fascinating complexity as the shape of a snow flake. In this case the interface is between the liquid and the solid which is in the process of solidifying into a dendritic crystal. Interesting pattern formation also occurs between two dissimilar fluids with different viscosities when the less viscous fluid pushes into the more viscous one. Such patterns are found in Hele Shaw cells and specifically in the Saffman-Taylor geometry studied in depth by the groups of Kadanoff and Libchaber. Patterns are also found in simple dynamical systems where there has been considerable effort comparing theory and experiment. The work at Chicago has been concerned with the analysis of the fractal attractors generated at the onset of chaos in convective flow experiments in the Rayleigh Benard geometry. This work, led by the groups of Halsey, Kadanoff and Libchaber, has had input from a number of MRL supported visitors. One of the ways that this Thrust Area has been developing has been in the study of patterns formed in a variety of new systems. Thus soap froths (or foams) and the interface between two phases of a liquid crystal have also been investigated. In the latter work, the experiments have been analyzed with the aid of theories developed by Goldstein and Gunaratne. New work on patterns formed by crack propagation has also been initiated by

Halsey and work on non-linear current paths has been investigated by Fritzsche under the present MRL grant.

A related development in the few years was the idea of self-organized criticality introduced by Bak, Tang and Wiesenfeld. There the hypothesis was that a system, such as a pile of sand, would organize itself in such a way that when it reaches steady-state conditions it is unstable to small perturbations, such as adding another grain of sand. The processes that result, such as landslides, are predicted to be critical in that they occur over all length scales and have a fractal shape. The Chicago MRL has started to study these ideas in depth. Kadanoff and Nagel are involved in studying simple cellular automata models of these "sand piles". In parallel, Nagel, Witten and Jaeger have studied the flow of real sand. In this work, the emphasis is again on the interface, which in this case is the surface of the sand pile.

A question naturally arises from what we have mentioned so far: what processes prevent pattern formation? As a liquid is cooled will one always get an interface between the growing solid region and the liquid surrounding it? Clearly this will not always happen. As a liquid is supercooled below its equilibrium freezing temperature it may either nucleate and crystallize or else it may form a glass. The nature of the glass transition has been a matter of vigorous debate for over forty years. Is it a phase transition or is it simply a kinetic slowing down of the liquid? In the University of Chicago MRL this question has been studied intensely by many investigators over many decades. M. H. Cohen worked on this question from the free-volume point of view in the 1960's. More

recently Freed, Mazenko, Nagel, and Oxtoby have collaborated on trying to address various aspects of this problem. Clearly this line of research has much in common with the work described in Thrust Area II on Disordered Materials.

This Thrust Area is a special blend of theorists and experimentalists working on problems at the cutting edge of materials science. Sometimes a single idea can serve as a unifying feature to bring together several approaches from many areas of materials science. One example is the concept of multi-fractality which entered our lab through the work of Halsey on models of aggregation. More recently, this idea has been applied to the analysis of data from the dynamical systems experiments of Libchaber and of Paul Linsay (MIT), to the study of sand pile simulations (Nagel and Kadanoff), electrodeposition (Halsey), of convective turbulence (Libchaber and Kadanoff), and has been proposed as a possible mode of analysis of relaxation phenomena in glassy systems (Kadanoff and Nagel).

I. DYNAMICAL PATTERNS

Introduction: The faculty leaders in this thrust area are Thomas Halsey, Sidney Nagel, Albert Libchaber, Hellmut Fritzsche and Leo Kadanoff. They are trying to use MRL support in conjunction with support from other sources to build a distinctive effort in which theory, simulation and experiment work together to build explanations of how non-trivial patterns are built up in condensed matter systems.

A. MULTIFRACTAL CORRELATIONS

In recent years, our understanding of how to describe the quantitative structure of patterns such as the surface of a growing viscous finger or electrodeposit or the region of maximum dissipation in a turbulent flow has been considerably improved. Halsey and Kadanoff have, in collaboration with other workers, introduced a 'multifractal' formalism for describing the types of universality and scaling behaviors found in these types of systems.¹

Halsey, in collaboration with the student Lee, has recently extended this formalism by studying the behavior of two-point correlations with distance in a multifractal system.² They succeeded in understanding the relation between the 'multifractal' exponents and the behavior of correlation functions of restricted regions of a multifractal system.³ As an example, their method allows one to relate the correlations of the most dissipative regions of a turbulent flow with the scaling properties of moments of the dissipation.

This work on multifractals has formed the basis for a considerable work on the analysis of experimental data for convective flow, self-organized criticality, and turbulence (see below). We even hope to apply it to glassy dynamics.

B. THE DESCRIPTION OF CHAOTIC BEHAVIOR IN CONVECTIVE FLOW

This is a joint project of Thomas Halsey's Leo Kadanoff's and Albert Libchaber's groups, with the major scientific work having

been carried out by a large group of visitors, research associates and students.⁴ During the past years, we made a major effort in the comparison of theory and experiment in the measurement of fractal properties of attractors in simple dynamical systems. The basic idea was to use the data generated at the onset of chaos in convective flow in the Rayleigh Bénard geometry to test the notion of Feigenbaum and others that there were a few universal routes to chaos in low dimensional dynamical systems. We have studied two such routes in considerable detail: the period doubling scenario and the quasi-periodic one. In both cases, we measured the spectrum of fractal dimensions of the attractors (f versus α) and found that to, within a few percent, these spectra were identical to the ones predicted theoretically. This work is now complete.

More recent work involves the comparison of the observed behavior in the chaotic region with theory. The chaotic region is crossed by an infinite number of periodic regions, which overlap in a well defined pattern.⁵ We have been able to undertake a full examination of the transition to intermittent chaos. These investigations has been carried out in both a mercury convection cell and in an electronic resonator system. The MRL portion of the work involved testing the theoretical predictions against the Chicago experiments. This too is now completed.

C. HELE-SHAW CELL STUDIES

There has been an ongoing and close collaboration between the experimental group of Libchaber and the theory group of

Kadanoff on moving interface problems in Hele-Shaw cells. This cell is one in which two fluids are confined between two narrowly spaced flat glass plates, giving, to a very good approximation, a two dimensional flow. The interface is then studied as the front advances under some driving force. A variety of aspects of the problem have been worked on here at Chicago, including connections to DLA,⁶ new families of analytic solutions,⁷ three dimensional effects,⁸ solidification problems⁹ and ones involving liquid crystals. This work is now substantially complete.¹⁰

D. A MACROSCOPIC MODEL OF 'GLASSY' DYNAMICS

Professors Nagel, Kadanoff, Libchaber and Witten are collaborating on a program in which they are looking at motion of granular materials subjected to external forces. This subject has both engineering and scientific importance. On the engineering side, many technologies depend on the efficient handling of powders (e.g., pharmaceuticals, grain, etc). On the scientific side, it is observed that granular materials (e.g. sand) have a dynamics which shows long-time tails, stretched exponentials, and other glass-like behavior. Hence they may serve as accessible (and macroscopic) models of the microscopic dynamics of glassy materials. This work started as a further investigation of the simulations of Bak, Weisenfeld and Tang.¹¹ The result of the simulation carried out by Kadanoff, Nagel, Wu and Zhou¹² include three rather unexpected features: The first is that the probability distributions can be better described by multifractal distributions than by ordinary scaling theory. The second is that there are many

different non-trivial universality classes among the sand-slide models. The third is that there are non-trivial models in one-dimension.

In a series of experiments Nagel¹³ and his group have been measuring the distribution of land slides in a pile of sand.

In the first experiment the sand grains are dropped onto a platform at a very slow but steady rate. When the sand pile has reached its steady-state height, sand will fall off the edge as new grains are added at random on the pile. A capacitor, located just below where the sand falls off the platform, detects the number of grains that fall as a function of time. A signal analyzer is used to calculate the power spectrum of the sand current. These experiments have been done with sand particles of different size and with sand particles of different shape. It is of interest to see if the characteristics of the slides are influenced by the shape of the particles (i.e., see the effect of replacing the rough grains of sand by spherical glass beads). To insure that the feeding mechanism (i.e., the way the sand is added to the pile) does not influence the results, they have also done a related experiment with a rotating drum filled with sand. The drum is rotated very slowly so that the angle is kept close to the "angle of repose" that is the critical angle. In this case it is not necessary to introduce more sand into the system and therefore the characteristics of the feeding mechanism are irrelevant.

These experiments indicate that the situation of real sand is quite different than was proposed in the models of Bak, Weisenfeld, and Tang.¹¹ The most obvious difference is that there

are two different "critical" angles. The sand pile will build up to an angle θ_1 without any appreciable landslides at all. When sand is added (or the drum rotated) above this angle the pile will collapse to another angle, θ_2 . This collapse occurs in one global, system-spanning, avalanche. The time between avalanches is proportional to the difference ($\theta_1 - \theta_2$). Another experiment is to see what effect noise (i.e., vibrations) have on the landslide spectra. When vibrations are introduced to the sand-pile the power-spectrum of the sand falling off the pile becomes much more complicated. It becomes possible to have slides which have many more length (or time) scales. However, even in this case it has not been possible to see a single power law which covers the entire range of timescales.

In order to test whether the landslides are determined only by the surface dynamics or whether strains in the bulk are also important, Nagel's group has studied the effect of piling up the sand on an inclined plane instead of on a flat surface. They found that many of the phenomena that they observed for the full pile (i.e., for the case where the bottom was horizontal) were also seen in the case where the bottom was tilted. This indicates that the landslides are occurring due to motion within a few layers of the top surface. This can be seen also by observing the existence of a boundary layer where all the motion occurs.

In parallel, Professors Nagel and Kadanoff¹² have been involved in a series of simulations of simplified models of avalanches. The basic starting point was a series of papers by Bak, Weisenfeld and Tang¹¹ in which they suggested that $1/f$ noise might be a universal phenomenon arising from a natural tendency

toward marginal stability in non-equilibrium systems. They gave several models which display this behavior, including a few which might describe simplified versions of sand slides. The work in the Chicago MRL was designed to test a variety of models to see their temporal behavior and to test their scaling and universality properties.

One model which was studied involved a model in which a sand pile is expressed in a lattice model by giving the height, $h(j)$, of a stack centered at j . The model involves two kinds of steps: an addition step which simply chooses a j -value at random and adds one grain to that stack: $h(j) \rightarrow h(j)+1$. Then if the slope of the pile is sufficiently large the sand starts to slide. One step of the slide will occur whenever $(h(j) - h(j+1)) > 2$. In that case, two grains will fall and, in the model which we propose to use, $h(j) \rightarrow h(j)-2$ while $h(j+1) \rightarrow h(j+1)+1$, and also $h(j+2) \rightarrow h(j+2)+1$. This slide can cascade.

They have studied this and similar models in one and two dimensions. They noticed that the length of the cascade shows long-time tails. The analysis seems to show a complex behavior, with several different universality classes. The present results indicate that the one-dimensional slides have a multifractal character whereas the two-dimensional models seem to be adequately fit by scaling behavior.

E. FRONT INSTABILITIES IN LIQUID CRYSTALS INTERFACES

The dynamics of moving interface between a solid and a liquid is a richly nonlinear problem that has been studied for many years. In "directional solidification" experiments, the interface is forced to move by translating a sample through a temperature gradient that is fixed in space. As the imposed velocity is increased, the uniform planar state gives way to a periodic "cellular" pattern. An example of such a pattern is the case of an interface between the isotropic and nematic phases of a thin sample of a liquid crystal. These particular directional solidification experiments¹⁴ were carried out at the University of Chicago by John Bechhoefer (now at the Ecole Normale Supérieure in Lyon, France), Albert Libchaber, Patrick Oswald (also now in Lyon), and Adam J. Simon.

The dynamics of this Mullins-Sekerka instability¹⁵ are well understood to arise from a competition between surface tension, which acts to damp undulations, and diffusive effects which force fluctuations to grow. An essential aspect of the theoretical treatment of this instability is the recognition of the basic symmetries and invariances of the periodic pattern. For instance, the pattern is left-right symmetric. Indeed, this "parity" symmetry is known to extend quite far beyond the onset of the basic cellular pattern, and is implicitly assumed to exist in most theoretical treatments. Symmetry considerations such as these are very powerful, and are often sufficient to describe universal aspects of such cellular instabilities. Recent experiments¹⁶ by Simon, Bechhoefer, and Libchaber have yielded surprising results. They see that there is a

localized traveling region in which the pattern has a markedly altered asymmetric shape. These traveling domains possess remarkable properties. First, they may move across the interface pattern in either direction, but the characteristic asymmetry of the pattern within the domain is precisely related to the direction of motion. They generally leave in their wake a reflection-symmetric pattern with an altered wavelength, and the successive passage of these domains across the pattern relaxes the wavelength to a fixed value; that is, they act to select a pattern.

An explanation for these phenomena has recently been proposed¹⁷ by Pierre Coulet (Nice), Raymond E. Goldstein and Gemunu H. Gunaratne (Chicago). They suggest that these domains are nucleated inclusions of a pattern within which the left-right symmetry (or parity) is broken. Based on considerations of the remaining symmetries, they have suggested a model for the appearance and motion of these inclusions that offers an explanation for many of these new experimental observations. Since the theory relies only on very general symmetries and invariances, it might be expected that other nonequilibrium systems in one spatial dimension might exhibit analogous phenomena.

In fact, more recent studies¹⁸ of solidification in eutectic mixtures have yielded similar results, namely, the existence of so-called "tilt waves" that move across a banded pattern normal to the direction of motion of the advancing solid-liquid interface. Analogous observations have been made in studies¹⁹ of "directional viscous fingering," a phenomenon occurring on the meniscus of a

thin film of fluid near confined between two rotating cylinders of different size. Beyond a characteristic rotation speed, the horizontal liquid-vapor meniscus becomes unstable, forming a periodic array of Saffman-Taylor-like fingers. At still higher velocities, the system undergoes a second instability resulting in an asymmetric travelling-wave state. Finally, experiments²⁰ on Rayleigh-Benard convection in long, narrow channels also appear to show travelling asymmetric domains far beyond the initial instability.

In the proposed theory,¹⁷ the complicated pattern is resolved, as any asymmetric pattern may be, into a sum of symmetric and antisymmetric components. If we call the interface shape $U(x, t)$, then we have

$$U(x, t) = U_S(x + \phi) + AU_A(x + \phi),$$

where the symmetric pattern U_S is like that at the top left, say

$$a_1 \cos(q(x + \phi)) + a_2 \cos(2q(x + \phi)),$$

and the antisymmetric function U_A might be like $b_1 \sin(q(x + \phi)) + b_2 \sin(2q(x + \phi))$. The order parameter for the parity-breaking transition is then the amplitude A of the antisymmetric pattern, and has the form of an envelope function. The motion of the asymmetric domains is then reduced to that of the edges of the bubble.

The slow spreading of the width of these domains reminds one of the growth of liquid droplets in a supersaturated vapor, and it therefore suggestive to think of the parity-breaking transition as being like an equilibrium first-order phase transition, with the stable

value of A jumping discontinuously as a function of the control parameter in the experiment.

The dynamics of broken parity has been studied by means of so-called "amplitude equations" for the coupled time evolution of the amplitude A and the phase ϕ of the periodic structure, both presumed to vary slowly on the length scale of the cellular pattern.

The nonequilibrium nature of the experimental systems, e.g. a moving interface or convecting layer of fluid, suggests that these dynamics are, in general, *nonvariational*. That is, unlike systems relaxing to thermodynamic equilibrium where the free energy functional tends to a minimum, no such functional of the order parameter exists for this problem. It is precisely the nonvariational nature of the dynamics which leads to the propagation of the nucleated droplets of the antisymmetric state, and the associated wavelength selection and relaxation. For instance, bubbles of opposite parity (opposite values of A) move in opposite directions. The slow spreading of a bubble in turn is directly related to the wavelength selection that occurs in its wake.

More recent work²¹ has been concerned with understanding the defect structures of broken-parity states as well as the dynamics of collisions between localized domains. Experimentally, it is known that when two counterpropagating domains of broken parity collide, they annihilate each other, up to their difference in length. At the site of the collision new symmetric cellular structures are formed, implying phase singularities during the collision. This behavior has been shown to arise from a more complete theory of systems with

broken parity, a theory bearing a strong resemblance to that of time-dependent superconductivity.

F. PATTERN FORMATION IN ELECTROSEPOSITION

Several recent experiments have demonstrated that a wealth of different patterns can be formed in the electrodeposition of metallic ions from electrolytes. Sawada, Dougherty and Gollub, and Grier et al. have simultaneously reported a particularly provocative set of experiments. In these experiments, zinc deposits were grown radially from the cathode in zinc sulfate solutions.^{22,23} The solution was confined between closely spaced glass plates, creating an effectively two dimensional geometry. The types of deposits created were then investigated as a function of the concentration of the zinc ions in the solution and of the deposition potential.

A variety of different deposit morphologies were observed in different areas of the concentration-voltage phase diagram with contradicting results between the two groups. These morphologies included dendritic morphologies, with dendrites aligned along crystalline axes and extensive side-branching, "open" morphologies resembling diffusion-limited aggregates, and "dense radial" morphologies, which were circular at large length scales.

While there has been theoretical study of some of the issues presented by this embarrassingly rich phase diagram, no complete theory accounting for the entire phase diagram has yet been proposed.^{24,25} In part, this is because of the large number of

physical effects involved. Electrodeposition is a more complex process, both as regards transport in the electrolyte, and as regards the surface kinetics, than most pattern formation problems heretofore studied. Transport in the electrolyte proceeds not only by ionic diffusion, but also by migration in response to the electric field. At the surface, in addition to the usual effects associated with crystallization, there will be significant effects associated with the charging of the electrical double layer.²⁶ These surface effects in turn affect the transport, as the potential drop across the microscopic double layer will influence the electric field throughout the solution.²⁷ It has also been suggested that the electrical resistance of the deposited metal may be significant in some situations.²⁸

While the complexity of this problem makes it unlikely that the types of sophisticated mathematical treatment possible for the Saffman-Taylor problem will not be feasible here, the study of pattern formation in electrodeposition may still offer considerable rewards. Not only is electrodeposition a ubiquitous technological process, but also the very complexity of the problem suggests that some of the morphological solutions found by the growing electrodeposits may be of great intrinsic interest. Indeed, this appears to be the case in the experiment mentioned above.

Halsey has thus commenced a program of systematically analyzing the importance of the various physical effects in electrodeposition.²⁹ He has first studied the stability of a steadily growing flat interface under the assumptions that (1) surface tension is not significant (this is apparently true for a wide range of

concentrations in the experiments mentioned above). (2) There is no convective mixing in the solution, and (3) concentration gradients remain in steady state on time scales associated with changes in the shape of the surface. Although these assumptions, particularly the latter two, are not particularly physical, the results of this calculation were nevertheless quite interesting.

The most significant result of this calculation was the discovery that non-linear effects in the electrical double layer (such effects appear in, e.g., the Butler-Volmer equation for deposition rate as a function of potential across the double layer) can significantly alter the form of the morphological instability of a flat surface. In particular, while the standard Mullins-Sekerka instability involves a growth rate of perturbations that is linear in the wave vector of the perturbation (until cut off by the surface tension), this calculation resulted in a growth rate of that was *independent* of the wave vector of the perturbation over a wide range of length scales.³⁰ Clearly such effects could dramatically effect the morphology of a growing deposit.

More recently, Halsey, working in collaboration with his student Leibig, has developed a numerical algorithm for studying the growth of an electrodeposition model in which the effects of double layer capacitance are explicitly included. This method is closely related to a method for determining the frequency dependence of the double layer impedance at a rough surface.

G. ELECTRODEPOSITION

Halsey and Leibig have recently studied electrodeposition using a random walk algorithm closely related to diffusion-limited aggregation.³¹ Diffusion-limited aggregation with a sticking probability provides a stochastic model for electrodeposition with "secondary current deposition," a model of electrodeposition in which the solution is assumed to be well mixed, and in which the capacitance and surface kinetics at the double layer are treated in a linear approximation. They found that this model exhibits a crossover behavior, in which small scale morphologies resemble those of the Eden model, while large scale morphologies resemble those of diffusion-limited aggregation.³² Rather peculiarly, the crossover length between these two regimes depends not only upon the macroscopic length scales and parameters of the problem, but also upon the microscopic scales. This is actually in contradiction to the result obtained in linear stability theory for this model.

Halsey and Leibig have used a related algorithm to study the impedance at a fixed rough surface in the presence of a time-varying potential.³³ Their method allows one in principle to determine the geometric effects upon the impedance of an arbitrarily shaped electrode.

H. Si-H GLASS: METASTABLE STRUCTURES INDUCED BY LIGHT EXPOSURE

Normal glasses can be bought into various metastable configurations by quenching through the glass transition

temperature.³⁴ The relaxation towards a free energy minimum proceeds then by dispersive diffusion of the mobile species.³⁵ The bonded hydrogen in hydrogenated amorphous silicon is a unique kind of glass which can be brought into metastable states not only by quenching but by electronic means or by light exposure below the glass transition temperature T_g . The value of T_g depends in turn on the position of the Fermi level E_F , decreasing from 200° C to less than 100° C as E_F is moved from the gap center toward the valence band.³⁵ This intimate interrelation of the electronic properties, the equilibrium state of the Si-H glass, and the kinetics of glass relaxation yields a fascinating variety of phenomena not seen in other glasses. Moreover, it allows the measurement of dynamical properties of the Si-H glass by sensitive electronic means.

We have been able to explain the metastable increase in the dark conductivity which is induced by a brief light exposure in doping modulated pnpn... multilayers by a photo-induced perturbation of the Si-H glass structure of the hydrogenated amorphous silicon layers.^{36,37} The phenomenon called persistent photoconductivity (PPC) was discovered in 1984 by Kakalios, et al.³⁸ By identifying the kinetics of creation and relaxation of the PPC effect with that of photo-induced metastable defects in p-type hydrogenated amorphous silicon and the Si-H glass kinetics we have found the origin of this effect.^{36,37}

I. DISPERSIVE NATURE OF GLASSY DYNAMICS IN HYDROGENATED AMORPHOUS SILICON

The stretched exponential time dependence (Kohlrausch dependence) of the relaxation of metastable glass states in hydrogenated amorphous silicon has been derived from the dispersive diffusion of bonded hydrogen.³⁵ The dispersive diffusion of hydrogen is believed to be related to a broad spectrum of Si-H bonding sites. The energies of occupied as well as of unoccupied, i.e. of potential H-bonding sites depend on the distribution of electrons in localized Si-Si bonding and antibonding states.³⁵ A metastable change in Si-H bonding configurations and hence of the H-glass can therefore be initiated by changing the electron distribution over these Si-Si states.

II. DYNAMICS OF SOLIDIFICATION

A. DYNAMICS OF GLASS FORMATION

The Chicago MRL has been very active in the study of the dynamics of glass formation. Nagel and his group have carried out studies of the structure and temporal behavior of thermal and acoustic properties of systems above the glass transition. Mazenko and coworkers and Oxtoby and Freed have worked on both fundamental theories of glass formation and connections with Nagel's experiments.

The subject of the glass transition is complex and there is a general confusion as to what is the best approach for studying the problem. If there is an underlying phase transition, it is surely

masked by kinetic effects. One of the theories of the glass transition is primarily applicable to polymeric glasses³⁹ while others, including the free volume theory,⁴⁰ are more readily applicable to metallic glasses. Is there one type of glass transition, or is the glass transition different in different types of systems?

Nagel and his group have been studying a variety of properties of liquids as they are cooled into an amorphous solid or glass. This has included a study of the temperature dependence of the structure of glasses through temperature across the transition,⁴¹ and more recently studies of the ultrasonic properties⁴² the shear viscosity⁴³ and the specific heat.⁴⁴⁻⁴⁷ Many different properties show relaxation effects as the temperature approaches T_g . For example, the specific heat anomaly, which is one of the identifying features of the glass transition, is very strongly influenced by the rate of heating or cooling of the supercooled liquid.⁴⁸ The slower one cools a liquid, the lower will be the apparent glass transition temperature. Nagel and his student, Norman Birge, invented a new method of measuring specific heat,⁴⁹ C_p , of viscous liquids which allowed them to measure its frequency dependence.⁴⁴⁻⁴⁷ They were able to cover a wide frequency range from 0.01 Hz to 5 kHz. They were thus able to measure both the real and the imaginary part (i.e., the in-phase and out-of-phase parts) of the specific heat and thus measure directly the spectra of enthalpy relaxations as a function of temperature.

In addition to the specific heat studies, Nagel and his group⁴² have looked at the propagation of sound in the vicinity of the glass transition. They found that the relaxation spectra for glycerol

measured by the ultrasonics could be fit by the same Vogel-Fulcher law as was used to fit the specific heat data. A scaling law :

$$f=f_0\left(\frac{T-T_0}{T_0}\right)^{-a}$$

was suggested by the mode-coupling theory of Leutheusser. This also gave an excellent fit to the data (also shown in the figure) but with a rather large exponent a ($a \cong 13$). The shape of the relaxation peaks, as a function of frequency, could be fit by a Williams-Watts (or stretched exponential) form. Again the parameters were close to those used to fit the enthalpy relaxation data. In another experiment, Jeong, a student of Nagel measured the frequency dependent shear viscosity.⁴³ This also obeyed the same Vogel-Fulcher (or scaling) law as was found for the ultrasonics and specific heat. However the distribution of relaxation times was slightly narrower than had been found in those experiments.

There was considerable optimism in the past few years that the mode-coupling mechanism of Leutheusser⁵⁰⁻⁵³ was relevant to the liquid-glass transition and inspired the power-law fits to data discussed above. It has now been generally accepted⁵⁴ that the work of Das and Mazenko⁵⁵ established that the Leuthusser⁵⁰ mechanism does not lead to a sharp glass transition and instead seems to describe a substantial slowing down of the system in the dense liquid near the region where a transition is predicted by the Leutheusser solution. Indeed the model discussed by Das, Mazenko, Ramaswamy and Toner⁵² and modified by Das and Mazenko^{55,56} appears to be a quite good starting point for understanding the

dynamics of dense liquids. It does not appear that the perturbation theory solution of the model introduced by these authors will lead to the very large activated growth in the viscosity associated with glass formation in laboratory systems.

B. DYNAMICS OF CRYSTAL NUCLEATION AND GROWTH

Oxtoby is studying the processes of nucleation and growth of crystals solidifying from the melt.^{57,58} An understanding of the nature of these processes on an atomic scale is of great importance, because they help to determine the microstructure of materials and their mechanical and physical properties. It is very difficult to obtain direct experimental evidence of the early stages of nucleation and growth, because these processes occur in the middle of a bulk medium and are visible only in late stages. In addition, computer simulations are difficult because nucleation is strongly affected by periodic boundary conditions,⁵⁹ and crystal growth studies on a computer can only be carried out at unreasonably large undercoolings. For these reasons, theoretical studies of crystal nucleation and growth are a very high priority.

Oxtoby has applied modern density functional methods to study nucleation and freezing. During the past year, he has investigated accurate, non-perturbative density functionals and applied them to the freezing of mixtures of hard spheres. In collaboration with Rosenfeld, he is applying a very powerful geometric approach⁶⁰ to these systems, in order to understand the fundamental factors that affect freezing. The first applications of

this approach have been made to the crystallization of colloidal suspensions that are composed of spheres of two different diameters. Oxtoby has calculated phase diagrams for such systems and compared them with experiments of Pusey (RSRE Malvern, U. K.). The initial results of both theory and experiment show that crystallization is most difficult and glassy states form most easily in the vicinity of deep eutectics, just as for metal alloys.

Oxtoby and Schofield are studying the interplay of order parameter dynamics and temperature changes in crystal growth. This is an extension of work by Harrowell and Oxtoby⁶¹ to include effects of heat flow during crystallization, and leads to coupled differential equations for order parameter and temperature. This model can lead to velocity selection, whereas earlier work on crystal growth that employed an infinitely sharp interface was unable to predict the effect of undercooling on growth rates. Oxtoby and Lowen⁶² have developed a new exactly soluble model for interfacial kinetics in which relaxation to a steady state can be studied for both conserved and nonconserved order parameters. The model also can be generalized to include additional order parameters.

III. SEED AREA: CONVECTIVE TURBULENCE

RESULTS TO DATE

We have been looking at data which is emerging from an experimental setup in which convective flow is set up in a low temperature helium gas. (The experiment was conducted by B.

Castaing, F. Heslot, and X. Wu under support from NSF-DMR.)⁶³ The Rayleigh number is proportional to density squared in this case. Since the density can be varied over five orders of magnitude, the appropriate dimensionless number, called the Rayleigh number

$$Ra = g \alpha \Delta L^3 / \kappa \nu$$

can be varied over twelve orders of magnitude! (Here g is the acceleration of gravity, α is the volume expansion coefficient of the Helium gas, Δ is the temperature difference between top and bottom of the container, L is a typical dimension of the container, and κ and ν are respectively the thermal diffusivity and kinematic viscosity of the gas.) The experimental results indicate a variety of chaotic and turbulent regimes. A combined theoretical and experimental project under the direction of Libchaber and Kadanoff involves specifically looking at the highest Rayleigh number regime, $6 \times 10^7 < Ra < 10^{15}$. In a major data analysis and theoretical effort, we saw simple scaling and universality in the overall flow properties in the higher portion of this regime, and constructed a kind of mean field theory for the overall flow properties.⁶⁴

The next step is to analyze in more detail the detailed temperature histories from the bolometers. The squared magnitude of the fourier transform of this data, called the power spectrum shows some universal and multi-fractal features. (Other multifractal behavior has been observed in studies of atmospheric behavior⁶⁵ and other systems).^{66,67,68} The controllability of the situation is much better in our case and this is the first time that multi-fractal behavior has been seen in power spectra. This

analysis is closely related to earlier multi-fractal analysis applied to DLA, to dynamical systems, and to sand-piles all of which are part of this thrust. In the near future we hope to extend this same line of thinking to glassy systems. Thus, in this feature the various parts of the thrust are investigating a set of related ideas.

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III. PROJECTS OUTSIDE THRUSTS

HIGH RESOLUTION ANALYTICAL ION MICROSCOPY AND FOCUSED ION BEAM MICROLITHOGRAPHY

PERSONNEL

Faculty

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Students

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The Focused Ion Beam Facility at the Enrico Fermi Institute, headed by Levi-Setti, has continued to carry out a diversified, cross disciplinary research program involving imaging microanalysis of materials at high lateral resolution, maskless focused ion beam microlithography and advanced microanalytical instrument development. A number of NSF-sponsored programs participate in the use and upgrading of the unique capabilities of this facility, specifically a DMR (Metallurgy) program, a DIR (Biology) program, the Science and Technology Center for Superconductivity and the University of Chicago MRL.

Concerning MRL-related activities, Levi-Setti has contributed to the program of Thrust Area II with studies of high- T_c superconducting ceramics that are not part of the STcS activities, as reported in the relevant section above. Furthermore, emphasis has been placed, in this initial period of the current MRL grant, to further develop ancillary instrumentation for the Focused Ion Beam Facility, essential for the implementation of the research program outlined in the original grant proposal. At the same time, interactions with MRL colleagues have been active, in particular in the area of FIB microfabrication of quantum devices. The following will illustrate progress and proposed continuation of research in several areas:

- i) Nucleation and growth of metal oxide films.
- ii) Upgrade of advanced instrumentation for materials research.
- iii) Focused ion beam fabrication of microscience devices.

i) Nucleation and Growth of Metal Oxide Films.

The discovery that Levi-Setti's high resolution ion microprobe is capable of monitoring with unprecedented detail the nucleation and growth of metal oxide films has been discussed in the main body of the current grant proposal. In summary, the oxidation of a liquid gallium surface, exposed to a controlled atmosphere of oxygen admitted into the vacuum chamber of the microprobe, was monitored by sequential SIMS mappings, using either the O- or the Ga⁺ secondary ion signals originating in the bombardment of Ga₂O₃ by the 40 keV Ga⁺ beam of the ion microprobe. The oxide film was observed to nucleate at the borders of an oxygen-free window, previously sputter-cleaned using the analyzing probe itself, and to grow, in the initial stages, in a fractal pattern characteristic of diffusion limited aggregation. By controlling the rate of oxygen accommodation on the Ga surface and the rate of oxide removal by sputtering, it was possible to arrest the growth of the oxide film and also to observe the process in reverse. From the signal intensity distribution along the growth pattern, and also from the observation of the regression of the growth under sputtering, it was possible to assess that the front of the growth is mostly two dimensional, most likely one monolayer thick. The oxide layer, however, grows in thickness as well as lateral extent. The fractal pattern of growth for the initial, monolayer phase, could be well modelled by computer simulations based on aggregation of two dimensional random walkers, up to fractal dimensions in the range 1.6-1.7. According to this model, the diffusion of oxygen adsorbed on the surface is believed to be the key to understanding the growth pattern in the

initial stages. Definite departure from this simple model occur for larger areal coverage, when other modes of aggregation come into play. These observations have been described in a comprehensive publication¹.

Toward the implementation of the next phase of this investigation, which contemplates studies of the temperature dependence of several aspects of the oxidation process, a temperature-controlled, cryogenic specimen stage has been constructed, which will replace the existing microprobe stage. The realization of this instrumental upgrade bears witness of the symbiotic relationship that has developed among Levi-Setti's Focused Ion Beam Facility, other MRL thrust areas, and the independently funded, cross-disciplinary programs that gravitate on the use of the Facility. In fact, this new instrumental addition was originally contemplated within Levi-Setti's biology program, funded by the NSF DIR, to carry out microprobe observations on frozen, hydrated specimens. As it turned out, need for the same stage has arisen in connection with the studies of high T_c superconductors, as mentioned in Thrust Area II, and its availability has given impetus to the proposal of experiments relevant to the topic under discussion in this section.

The new stage makes use of a VG high precision micromanipulator carriage to support a liquid-N₂-cooled Cu block. The latter carries a dove-tailed housing where the sample plug is inserted. Six electrical leads are provided to perform electrical measurements on a sample. The Cu block contains a thermocouple and a heater. A test of the system in a vacuum chamber showed

reproducible temperature control from room temperature to 78 K. It is also possible, without modification, to raise the stage temperature up to 200 °C. The entire system is mounted on a 8" UHV flange, so as to be interchangeable with the present carousel stage of the microprobe. This interchange will be scheduled as appropriate.

ii) Upgrade and development of advanced instrumentation for materials research.

Ion Microprobe Microprocessor Control. A radical upgrading of the UC Ion Microprobe control system was recently implemented. The microprobe was originally designed with a versatile, programmable, custom-build scan generator. This digital generator is potentially capable of scanning the probe over square or rectangular rasters while simultaneously controlling many additional variables such as rotation, astigmatism, skew, and alignment. Vector scanning is also possible.

To exploit these features, the scan generator must be controlled by a host microprocessor that satisfies three requirements: 1) The microprocessor must compute data for the appropriate addressable devices in the scan generator, in real time; 2) To reduce dead time, the microprocessor must send commands to the scan generator at a rapid rate; 3) Finally, the host computer must be reliable, not prone to catastrophic breakdowns, and easy to program.

Until recently, a 2 MHz, 8 bit Z80-based computer served as the control computer. The limitations of this system were deleteriously obvious. In order to reach the minimum speed requirements imposed by the scan generator, the Z80 was programmed in

impenetrable assembly language, making software modifications impossible. The slow clock speed also ruled out the implementation of computation-intensive tasks. Significantly, the computer was built using the archaic S-100 architecture, making repairs and additions difficult. This latter problem was most crippling, because the computer was experiencing almost daily failures.

With MRL support, Levi-Setti purchased a Macintosh IIX computer (15.7 MHz, 32 bit 68030 processor, math coprocessor, 80 Mbyte hard disk), a National Instruments 24 bit parallel digital interface expansion card, and a National Instruments 6 channel digital-to-analog converter interface card. Additional interface hardware was constructed to mate this hardware to the existing equipment.

The control software was written in the C programming language with the assistance of Richard Ernst (student, S. Nagel), and operates as a standard Macintosh™ application. This hardware-software combination is fully capable of controlling the more than 36 addressable devices in the scan generator, and performs real time trigonometric and scaling operations for advanced scan control. The program interface is "user friendly" and exceeds, by many standards, the functionality of commercially available software.

The Macintosh has also been interfaced to other instrumentation, improving the utility of the UC Ion Microprobe for advanced experimentation. A serial data transfer program was developed that transfers information from a multichannel scaler to the Macintosh, where statistical analysis and graphing can be performed easily. Also, a local area network has been established

through which images and microquantification data from the KONTRON image analyzer can be downloaded to the Macintosh for further analysis.

Mass-peak switcher. In another development, the RF quadrupole mass filter of the UC Ion Microprobe has been supplemented with a custom-designed mass-peak switcher. When appropriate trigger signals have been received, the peak switcher, using CMOS technology integrated circuit switches, rapidly tunes the mass filter through a sequence of up to four, preselected, mass-to-charge ratios. When used in conjunction with the digital image storage and processing system (acquired as described previously as part of Levi-Setti's DIR program), this circuit allows the acquisition of quasi-parallel multimass information during a single SIMS scan.

For example, by retuning the mass filter during every raster line retrace, interlaced images can be obtained which are then unscrambled to yield pairs of simultaneous, spatially self-correlated mass-resolved images. This method of obtaining isodepth multimass images² has attracted much attention in the SIMS community, since it allows the correlation of different compositional images resulting from a single scan, rather than from a series of sequential scans as usually required with a quadrupole system (when analyzing submicron-sized precipitates and particulates, a single scan is all that is allowed prior to the destruction by sputtering of the detail of interest). The peak switcher is also used to great advantage in the acquisition of multimass depth profiles.

iii) Focused ion beam fabrication of microscience devices.

Levi-Setti has continued to provide assistance and collaboration to MRL colleagues and students, through the use of his Focused Ion Beam Facility. An ongoing effort, undertaken in collaboration with Richard Ernst of Nagel's group, involves the microfabrication of quantum wires.

Very small metallic wires, when cooled sufficiently, can begin to exhibit manifestly quantum mechanical behavior due to electron interference effects. Micron scale wires measured at dilution refrigerator temperatures ($< 1\text{K}$) show characteristic fluctuations in conductance of order e^2/h as a function of many controllable parameters, e.g., magnetic field. As part of this investigation, it is hoped to determine the sensitivity of such fluctuations to the microscopic distribution of scattering centers by measuring the conductance of a sample subject to radiation damage. Using the Focused Ion Beam Facility, a technique for fabricating metallic wires with dimensions down to $5\mu \times 0.5\mu$ has been developed. The procedure involves ion lithography, using a poly-methylmethacrylate (PMMA) resist, the ion probe as an exposure source, and an organic solvent developer. Glass substrates are first coated with a thin layer of PMMA, and are then exposed using the ion probe. By controlling the beam positioning by means of the microprobe's KONTRON image display system used as a pattern generator, it is possible to expose any desired pattern. PMMA bombarded by the ion beam is more soluble in an organic developer (a mixture of methyl-isobutyl ketone and isopropanol) than unexposed PMMA, so that the development process uncovers bare substrate in places where the beam has hit.

The final step in the fabrication process is to deposit the metal film, which can be done through either vacuum evaporation or DC sputtering.

Thus far patterns with features down to 0.5μ have been successfully produced, and the ultimate limit for this process (using a single layer of PMMA) is probably about 0.1μ , should the need arise for devices of that size in the future. Apart from quantum wires for conductance fluctuation experiments, this ion lithography process has been employed to fabricate superconducting loops for a SQUID-based experiment, and serpentine heater films for a variety of studies.

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IV. COMMON FACILITIES

The eight Common Facilities play an important role in our Materials Research Laboratory. Very often the interactions that take place within these Facilities lead to the collaborative efforts between different faculty members, which is the hallmark of our MRL program. In addition, it is the training which occurs within these laboratories which help to give our students a broad interdisciplinary outlook on Materials Research and help to pass on technical know-how from one generation to the next. Each of our facilities is headed by a professional staff member and supervised by someone from the MRL faculty. The staff member is instructed not only to maintain the equipment up to specifications and to do some of the routine measurements or preparations, but also to help train the students, research associates and faculty to use the equipment themselves.

During the past two-and-a-half years there have been a number of major changes in our MRL Common Facilities. These are outlined below in some detail, but we will give a brief overview here. In conjunction with the James Franck Institute we have found more and better space for housing some of the laboratories. For example, the Computer Facility is moving into larger renovated space in order to accommodate the increased use that has occurred over the past few years. Several Facilities have been moved into newly renovated "clean room" space so that they are now contiguous to one another. Thus, the Materials Preparation and Spectroscopic Facilities and the Electronics

Shop now occupy adjacent rooms, which has allowed a pooling of resources. Of primary importance, of course, is that this move provided clean room space for those facilities that needed it. These improvements were made after lengthy consultations with the MRL faculty to see which capabilities needed to be improved, and after negotiations with the University Administration, who agreed to pay for the renovations and provide the MRL with new space.

Perhaps the largest change occurred in the Spectroscopic Facility where a Brillouin Scattering Spectrometer has been added to enhance our vibrational spectroscopy needs. In the near future we would like to expand this facility even further with the addition of a new Fourier Transform Infrared Spectrometer, and possibly the addition of a Fourier Transform Raman Spectrometer as well.

NSF core funding provides about 50 percent of the service salaries for our professional and technical staff, as well as for providing major equipment items. As one can tell from our items of requested equipment in Table 1, much of the equipment we are requesting is for the Common Facilities. The remainder of the operating cost is covered by hourly service charges, University funds, and funds from individual contracts. The Materials Research Laboratory supports the following facilities:

1. Chemical Analysis and Synthesis Laboratory
2. Computer Facility
3. Electronics Shop
4. Low-Temperature Laboratory
5. Materials Preparation Laboratory
6. Microanalytical Facility

7. Spectroscopic Facility
8. X-ray and Neutron Scattering Facility

In addition to these supported Facilities, the Materials Research Laboratory profits from the availability of the Synchrotron Radiation Facility at Stoughton, Wisconsin, and the Intense Pulsed Neutron Source and other specialized capabilities at Argonne National Laboratory. Moreover, several important equipment items, which remain under the supervision of individual faculty, are available to MRL researchers.

1. Chemical Analysis and Synthesis Laboratory

Faculty Supervisor: Professor O. J. Kleppa

Technical Staff: Dr. A. Davis

This laboratory provides faculty members, research associates, and graduate students with basic qualitative and quantitative chemical analyses of samples. Services provided by the laboratory include: (i) quantitative inorganic chemical analyses, (ii) inorganic material identification, and (iii) inorganic synthesis at high temperatures.

Quantitative chemical analyses are now done with an atomic absorption spectrophotometer, using flame atomization for most analyses and graphite furnace atomization for samples with low concentrations of certain elements. The instrument used is a Perkin-Elmer 306 atomic absorption spectrophotometer with an HGA-2100 graphite furnace. There are hollow cathode lamps available to determine 47 different elements. The laboratory also contains a Rigaku differential thermal analyzer-thermo-gravimetric analyzer-differential scanning calorimeter.

The laboratory is equipped with a variety of furnaces for high-temperature syntheses. 1984-85 funds were used to purchase a Deltech DT-31-RS-OS-VT vertical tube furnace with a 2-1/2" OD opening. This furnace is capable of routine operation at 1700°C and can go to 1725°C for short periods of time. The laboratory is also equipped with a globar-heated muffle furnace (1500°C maximum) with a programmable temperature controller, a CM 3-zone 5" diameter

crystal-growing furnace (1000°C maximum), and a Charles Engineering Co. crystal-growing furnace (1000°C maximum).

In addition to his duties in the Chemical Analysis and Synthesis Laboratory, Dr. Davis is responsible for the operation of a scanning electron microscope located in the Department of the Geophysical Sciences. It is a JEOL JSM-35 equipped with a backscattered electron detector and a Si-Li solid state X-ray detector connected to a Kevex 7000 System 77 quantitative analysis system. The instrument was purchased several years ago by four University of Chicago faculty members (E. Anders, R. N. Clayton, L. Grossman, and J. V. Smith) and E. Olsen of the Field Museum of Natural History, and it is operated on a zero-ledger account. MRL members have access to this instrument through Dr. Davis, and MRL pays for the time used. This scanning electron microscope has proven to be very useful for characterizing many MRL-related samples. Subtle chemical zoning effects can easily be imaged using the backscattered electron detector. Quantitative analyses of all elements from Na to U at levels as low as 0.1 wt% can be made on areas as small as 1 micrometer across. This instrument is also extremely useful for rapid characterization of small unknown samples, a task that was once done with much more difficulty by DC arc emission spectrography.

2. Computer Central Facility

Faculty Supervisor: Professor L. Kadanoff

Computer Specialist: Mr. Su-min Zhou

The MRL's Computer Facility is designed to permit users to work interactively with a variety of computers on our campus and elsewhere. We have been especially interested in making good graphics available to our users.

The facility includes five SUN workstations, five printers capable of graphical output, five terminals connected directly to the SUNs, five Macintoshs (including two Macintosh II's), and a Hewlett-Packard Series 9000 model 330. The workstations operate from a SUN 3/160 file server which has two 380 megabyte disk drives. This enables a user to access the same files no matter which workstation is being used. The Macintosh network is connected to a Kinetics gateway allowing users to connect instantly via the ethernet system to any of the University's computer systems as well as many systems nationwide. Likewise, the SUNs and the H-P are connected to the University's other systems. The theorists mostly use the SUNs, while experimentalists use the H-P equipment.

3. Electronic Laboratory

Faculty Supervisor: Professor R. Gomer

Technical Staff: Messrs. D. Smith, G. Jendraszkiewicz and B. Goers

The Electronics Lab. provides both repair and equipment construction services for the MRL faculty. Electrical and electronic equipment of the facility's members are maintained and repaired as quickly and reliably as possible. In addition, specialized electronic instrumentation needed by the members is designed and constructed by the lab staff. The lab's capabilities include both analog and digital instrumentation for signals in the frequency range D.C. to 1 GHz and voltage levels ranging from microvolts to kilovolts. A thorough documentation file is maintained for all constructed equipment.

In the recent past the lab has designed and constructed circuitry for the power and timing stabilization of lasers, a computer control interface for an electron energy spectrometer, control circuitry for an ion microscope, and a high-frequency quadrature signal demodulator.

The lab also maintains a pool of equipment for use by facility members. In addition to the usual meters, oscilloscopes, and signal generators, the lab has a 1 GHz microchannel plate oscilloscope for viewing fast transient signals, a logic analyzer, and a dynamic signal analyzer. A PC-AT type computer is available with software and hardware for the programming of programmable logic devices. Software for the generation of schematic diagrams and printed circuit artwork is also available.

The staff of the lab also acts in an advisory capacity to the members of the facility. Faculty and students are free to consult with

the staff on problems they may have regarding electronics. In addition, Mr. Jendraskiewicz has the responsibility of maintaining the evaporation equipment in the Materials Preparation Laboratory and to training students in the use of this equipment.

4. Low-Temperature Laboratory

Faculty Supervisor: Professor T. Rosenbaum

Technical Staff: Messrs. R. Szara, F. Gaca, and M. Pearson

The Low-Temperature Laboratory provides and stores cryogenic fluids, maintains leak testing equipment, constructs new cryogenic facilities, and oversees the general use of two helium dilution refrigerators. The original top-loading dilution refrigerator routinely cycles between .007 and 1 K, with magnetic fields up to 100 kOe. Total turn-around time for removing one sample, loading a new sample and cooling it to base temperature is less than six hours. The flexibility of this system has allowed a wide range of materials studies, with particular emphasis on Disordered, Superconducting, and Glassy Systems. This facility already has become oversubscribed. Hence, a second smaller dilution refrigerator was purchased with support from MRL and has been operational for almost two years. In addition, the increased use of the Low-Temperature facility has necessitated the services of a second technician, M. Pearson. He is being trained in cryogenic techniques and will help insure the continuity of expertise in low-temperature physics.

The Low-Temperature Laboratory is equipped with a CTI 1400 Helium Liquefier with built-in automatic refrigeration purifier. This

permits the recycling of helium used in experiments. The liquefier also contains a modification which enables the condensation and catalyzation of hydrogen, producing liquid parahydrogen. These cryogenic liquids are kept on hand at all times for experimentalists to use at will. Liquid nitrogen is also made instantly available. It is stored in a Linde TL 6000 tank of 24,000 liter capacity. The liquid is piped into a dispensing area which is equipped with electrically operated dispensing valves. Last year, 28,779 liters of liquid He, 1,614 liters of liquid H₂, and 261,023 liters of liquid N₂ were dispensed. These liquids are sold to MRL members and non-members to recover production and storage costs. The Laboratory has a recovery system for He, a safety system for H₂, and centralized pumping stations for temperature reduction of the cryogenic liquids used in experiments. The organization of the Laboratory is such that new experiments can be initiated without difficulty.

The technical staff of this facility designs and constructs cryogenic equipment and provides technical consulting. Students are instructed in cryogenic techniques. In addition, vacuum systems and leak detectors are maintained, and gas handling systems, automatic cryogenic liquid fill devices, transfer tubes, portable vacuum systems, and custom racks for experimental equipment are built within the Low-Temperature facility.

During the past two-and-a-half years the MRL administration has heavily subsidized the cost of liquid helium to MRL members. The rationale has been to encourage the doing of experiments over, for example, the building of equipment.

5. Materials Preparation Laboratory

Faculty Supervisor: Professor H. Fritzsche

Technical Staff: Mr. G. Jendraszkiewicz

In the past year, the Materials Preparation Laboratory was moved to new "clean room" space made available by renovations within the James Franck Institute.

Recent additions to the Materials Preparation Laboratory are a shuttered as well as a two-chamber plasma deposition system that enable one to make compositionally-modulated, as well as doping-modulated superlattices of amorphous semiconductors. The Materials Preparation Laboratory is further equipped with rf and dc sputtering systems with an assortment of target materials, and several multiple source evaporation and rf plasma assisted chemical vapor deposition systems for thin film preparation. It has induction-heating power supplies and electron beam systems with associated vacuum systems for melting, sintering, brazing, outgassing, and evaporation. There are available drying ovens, tube furnaces, muffle furnaces, an arc melting furnace, and a rocking furnace. It has available a Tolansky interference angstrom thickness meter, a Sloan Dektak surface profiling meter, an accurate dew point meter, several quartz crystal microbalances, and a residual gas analyzer. It has metallographic equipment for cutting, polishing, and machining, and apparatus for ultrasonic cleaning and spark erosion cutting. This latter equipment is placed in the Central Shop outside the clean room area.

A recent addition to the Materials Preparation Laboratory is a facility for photoresist masking and etching. Plans for the immediate

future include the acquisition of the necessary equipment for preparing thin sections of materials for transmission scanning electron microscopy.

All material preparation and *in situ* characterization done by the Disordered Materials group are carried out in this laboratory. There is no hourly charge, but the users provide the cost of materials. Due to the retirement of D. Dennison, the metallurgist who ran this facility, and due to the cuts in our MRL budget over the last year, G. Jendraszkiewicz of the Electronics Shop is temporarily taking over the job of directing this facility.

6. Microanalytical Facility

Faculty Supervisor: Professor J. Burdett

Technical Staff: Drs. I. M. Steele, M. L. Rivers, S. R. Sutton, and Mr. O. Draughn

This facility is expanding to take advantage of new opportunities. Most of the analyses will continue to be made with an electron microprobe, but there will be a major effort to develop new instruments, of which an X-ray fluorescence microprobe and a proton microprobe are of immediate importance.

An Applied Research Laboratory electron microprobe (vintage 1967) has been rebuilt over the past ten years in our workshops and still gives excellent service. It offers solid-state detector and spectrometer analyses with on-line computer automation. The extensive library of standards allows accurate analyses of all elements from Na to U and less accurate analyses for some elements below Na. The SX-50 instrument was delivered in June 1986, and works well. Particular emphasis is being placed on the cathodoluminescence (using a Princeton cathodoluminescence spectrometer) and secondary-electron capabilities in relation to precise measurement of minor and trace elements. The new instrument has demonstrated an SEM capability sufficiently good for the study of almost all multiphase specimens in the MRL program.

7. Spectroscopic Central Facility

Faculty Supervisor: Professor D. Heinz

A portion of the central spectroscopic facility has been moved to a new location in order to take advantage of new clean room space made available by renovations in the James Franck Institute. The facility has been reorganized around vibrational spectroscopy at extreme conditions. The equipment in this facility consists of a Raman spectrometer (purchased in 1979-80), an IR grating spectrophotometer with reflectometer attachment, a near IR-visible-near UV spectrometer, and a Brillouin spectrometer.

This equipment is designed to accommodate high-pressure, high-temperature diamond anvil cells, as well as samples at ambient conditions. Provisions have been made for future expansion to enable measurements at cryogenic temperatures which can also be conducted at high pressures. The facility will enable us to study vibrational characteristics of materials as a function of temperature and pressure and to observe the vibrational behavior at phase transitions.

An electron-spin resonance spectrometer (purchased with 1977-78 funds) and ancillary apparatus such as cryostats, oven high-pressure optical cell, etc. remain in the previous location. The ultrasonic spectrometer (built in 1980-81) is a portable unit which can be moved to different experimental setups. This apparatus can cover the range 1-100 MHz in a rapid manner (without the need to change transducers or electronics).

8. X-ray and Neutron Scattering Facility

Faculty Supervisor: Professor J. Burdett

Technical Staff: Dr. J. Pluth

The X-ray diffraction facility has played a key role in the research and teaching activities of the Division of Physical Sciences for the past two decades, and is now being expanded to cover the new opportunities offered by the intense tunable X-ray beams from synchrotron storage rings and by the intense pulsed neutron sources.

At the University of Chicago, the basic facilities are in routine operation. In the Hinds and Research Institute laboratories, the following major items of equipment are in use: automated Picker FACS-1 single-crystal diffractometers (completely rebuilt and automated to modern standards at about one-third the cost of the purchase of new instruments of inferior mechanical quality), Norelco powder diffractometers (one automated and interfaced to a computer); Buerger precession cameras and Weissenberg cameras, Guinier-de Wolff and Lenne high-temperature focusing powder camera, and Gandolfi powder cameras. Computer terminals in the Hinds Laboratory are connected directly with a shared VAX computer, and a complete range of programs is available.

Finally, the teaching program in X-ray and neutron scattering will be improved to take account of the major advances now taking place in theory and practice. Division-wide courses will be offered to provide a coherent development of the subject. They will be coordinated with courses on crystal chemistry and crystal physics.

APPENDIX 1

MATERIALS RESEARCH FACULTY, DEPARTMENTAL AFFILIATION (FEB 1, 1990)

	JAMES FRANCK INSTITUTE	DEPT. OF PHYSICS	DEPT. OF CHEMISTRY	DEPT. OF GEOPHYS.	ENRICO FERMI INSTITUTE
THRUST I. SURFACE DYNAMICS					
Prof. J. K. Burdett*	X		X		
Prof. U. Fano	X	X			
Prof. K. F. Freed*	X		X		
Prof. R. Gomer	X		X		
Prof. D. H. Levy	X		X		
Prof. J. C. Light	X		X		
Prof. G. F. Mazenko*	X	X			
Prof. S. A. Rice	X		X		
Prof. S. J. Sibener	X		X		
THRUST II. DISORDERED MATERIALS					
Prof. J. K. Burdett*	X		X		
Prof. K. F. Freed*	X		X		
Prof. H. Fritzsche*	X	X			
Asst. Prof. T. C. Halsey*	X	X			
Asst. Prof. D. L. Heinz				X	
Prof. O. J. Kleppa	X		X	X	
Prof. K. Levin	X	X			
Prof. R. Levi-Setti*		X			X
Prof. G. F. Mazenko*	X	X			
Prof. S. R. Nagel*	X	X			
Prof. R. C. Newton				X	
Prof. D. W. Oxtoby*	X		X		
Assoc. Prof. T. F. Rosenbaum	X	X			
Prof. T. A. Witten*	X	X			
THRUST III. - DYNAMICAL PATTERNS AND SOLIDIFICATION					
Prof. K. F. Freed*	X		X		
Prof. H. Fritzsche*	X	X			
Asst. Prof. T. C. Halsey*	X	X			
Prof. L. P. Kadanoff	X	X			X
Prof. A. J. Libchaber	X	X			X
Prof. G. F. Mazenko*	X	X			
Prof. S. R. Nagel*	X	X			
Prof. D. W. Oxtoby*	X		X		
Prof. T. A. Witten*	X	X			
HIGH RESOLUTION ANALYTICAL ION MICROSCOPY					
Prof. R. Levi-Setti*		X			X

*PARTICIPANTS IN MORE THAN ONE INTEREST GROUP

APPENDIX 2

PUBLICATION BY MRL FACULTY MEMBERS
ACKNOWLEDGING SUPPORT FROM MRL
During Present Funding Period

*Indicate publication acknowledged partial support from MRL.

**Indicate publication acknowledged primary support from MRL.

J. K. Burdett

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PH.D. RECIPIENTS, THEIR DESTINATIONS AND POSITIONS

Recipient	Sponsor	Destination and Position	Thesis Title
Bechhoefer, J.	Libchaber	Postdoctoral Ecole Normale Lyon, France	Directional Solidification at the Nematic-Isotropic Interface
Glazier, J.	Libchaber	Postdoctoral AT & T Bell Labs., Murray Hill, NJ	Dynamics of Cellular Patterns
Harris, J.	Rice	Postdoctoral AT & T Bell Labs. Murray Hill, NJ	Theoretical Studies of the Structure of the Liquid Vapor interface of Alkaline Metals and Alloys and the Structure and Phase Transitions of Supported Monomolecular Amphiphile Films
Koziol, A. M.	Newton	Researcher U.S. Geol. Survey Menlow Park, CA	Activity-Composition Relations of Selected Garnets Determined by Phase Equilibrium Experiments
Lai, Z.	Mazenko	Postdoctoral U. of Maryland College Park, MD	Theory of Ordering Dynamics for Cu ₃ Au
Reich, D.	Rosenbaum	Postdoctoral AT & T Bell Labs. Murray Hill, NJ	Glassy Dynamics of a Dilute, Dipolar-Coupled Magnet
Thomas, B.	Rice	Postdoctoral James Franck Inst. U. of Chicago	X-Ray Diffraction Studies of Liquid Surfaces