PUB-87, Rev. 1
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SURFACE AND CATALYSIS SCIENCE IN THE MATERIALS AND MOLECULAR RESEARCH DIVISION

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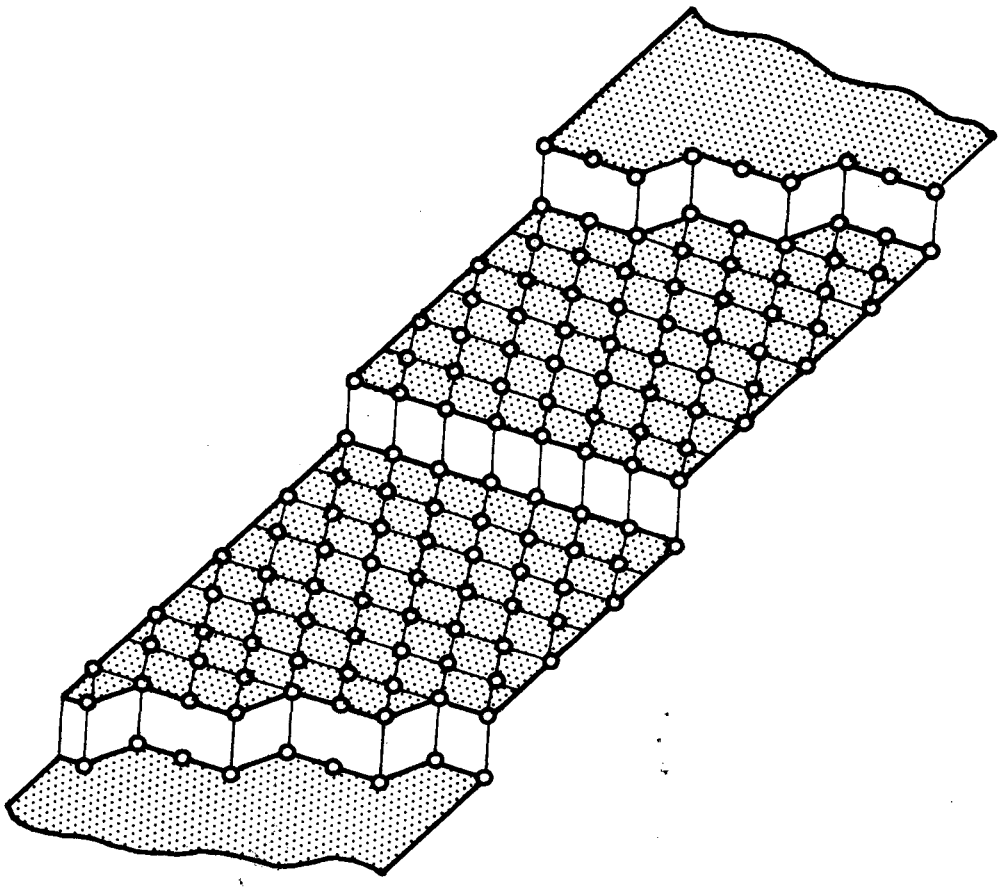

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INTRODUCTION

Many useful devices of our everyday life have very large surface areas that are necessary for their proper functioning. One example is our brain, perhaps one of the most complex devices we know. Others include the integrated circuitry utilized in electronic or computer technology, biological membranes, and the catalysts employed in most chemical technologies to aid in the production of chemicals or synthetic fuels at optimum rate and selectivity.

The very high surface-to-volume ratio of most of these devices makes it essential that we concentrate on the study of surfaces if we are to understand their operation. The purpose of our research at the Lawrence Berkeley Laboratory (LBL) is to explore the various physical and chemical properties of surfaces of different materials ranging from metals to organic polymers in order to understand and control their behavior. Thus, we study the atomic and electronic structure, the chemical composition, and the reactivity of different surfaces.

Surfaces have two essential functions that give them special importance:

1) They are the first line of defense of a solid or liquid against external attack by chemicals, nuclear radiation, or other hostile environments. Therefore, learning how to passivate a surface to protect the rest of the condensed phase against corrosion or erosion is one of our goals.

2) Surfaces that are not passivated are very reactive. Unique chemical reactions take place at the solid-gas or solid-liquid interface at a high rate and specificity not occurring elsewhere. Therefore, learning how to activate a surface to optimize the desired reactivity in chemical surface reactions is another important goal.

Some of the research areas that produce valuable information on the behavior of surfaces are described separately by topic.

Gabor A. Somorjai

THE STRUCTURE OF SURFACES: SURFACE CRYSTALLOGRAPHY

Principal Investigator: Gabor A. Somorjai

The purpose of these studies is to determine the arrangement of atoms in the topmost surface layer. The precise position and structural environment of surface atoms or molecules adsorbed on top of a surface reveals the nature of their chemical bonding that ultimately determines their behavior in chemical reactions.

Low-energy electron diffraction (Fig. 1) is the technique we use to determine atomic surface structure. In this research a monoenergetic beam of electrons in the range of 10 to 200 volts impinges on the sample crystal surface in ultrahigh vacuum conditions and the elastically backscattered electrons form a spot pattern indicative of diffraction from an ordered two-dimensional structure that is a single crystal surface on an atomic scale. A representative diffraction pattern is shown in Fig. 2. The incident beam energy can be easily varied. Analysis of the various diffraction spot intensities, as a function of the electron beam energy, yields the precise location of the atoms in the surface. Gases adsorbed on the crystal surface often form well-ordered domains, and the electron beam intensity data allow determination of the bonding geometry at the immediate interface of the solid and gas phases where heterogeneous catalysis takes place.

Research in this laboratory has developed a photographic technique that simultaneously collects the intensity data for all the diffraction beams in a few minutes; this overcomes many of the experimental difficulties of data analysis. The structure of several hydrocarbon molecules adsorbed on platinum surfaces was determined

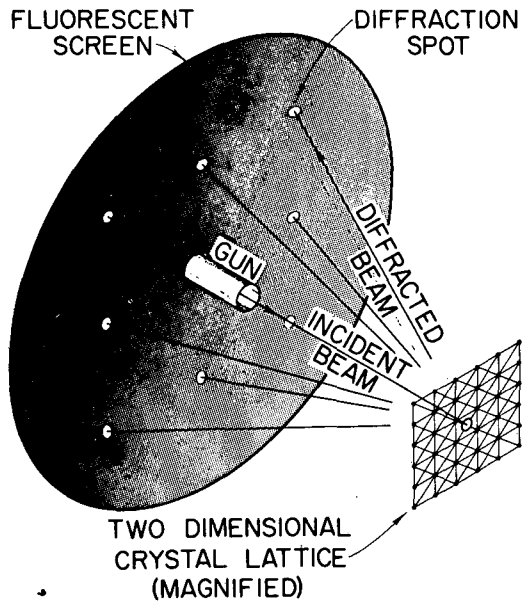


Fig. 1

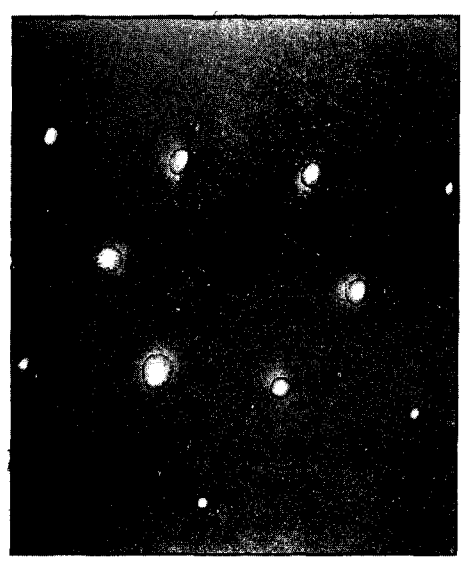


Fig. 2

this way. The location of one of these molecules, that of acetylene (C_2H_2), on the (111) crystal face of platinum is shown schematically in Fig. 3.

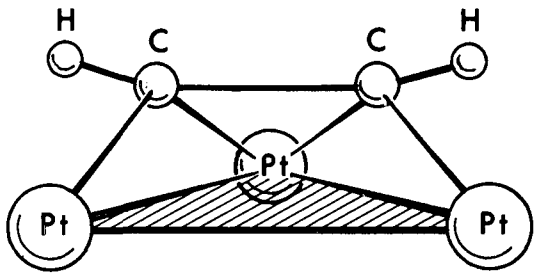


Fig. 3

The surfaces of organic molecules play an important role in many areas of biology and in polymer chemistry. We have been growing many types of organic crystals (hydrocarbons, amino acids, and metallo-organic compounds) and studying their surface structure by low-energy electron diffraction.

Surprisingly, atoms in the surfaces of many solids occupy atomic positions that are not expected from knowledge of their bulk crystal structure. These surfaces are designated as "reconstructed." Research is under way to determine the location of atoms in these reconstructed surfaces and the causes of these surface phase transformations.

Studies in this laboratory reveal that many surfaces exhibit a step-like atomic structure, such as those illustrated in Fig. 4. The terraces have widths that are determined by the method of preparation, and are separated by periodic steps one atom high. Our studies of adsorption and surface reactions on these surfaces reveal that chemical activity is very different at these surface irregularities. A systematic study of the chemical behavior of these imperfect surfaces explains the secrets of catalytic surface reactions.

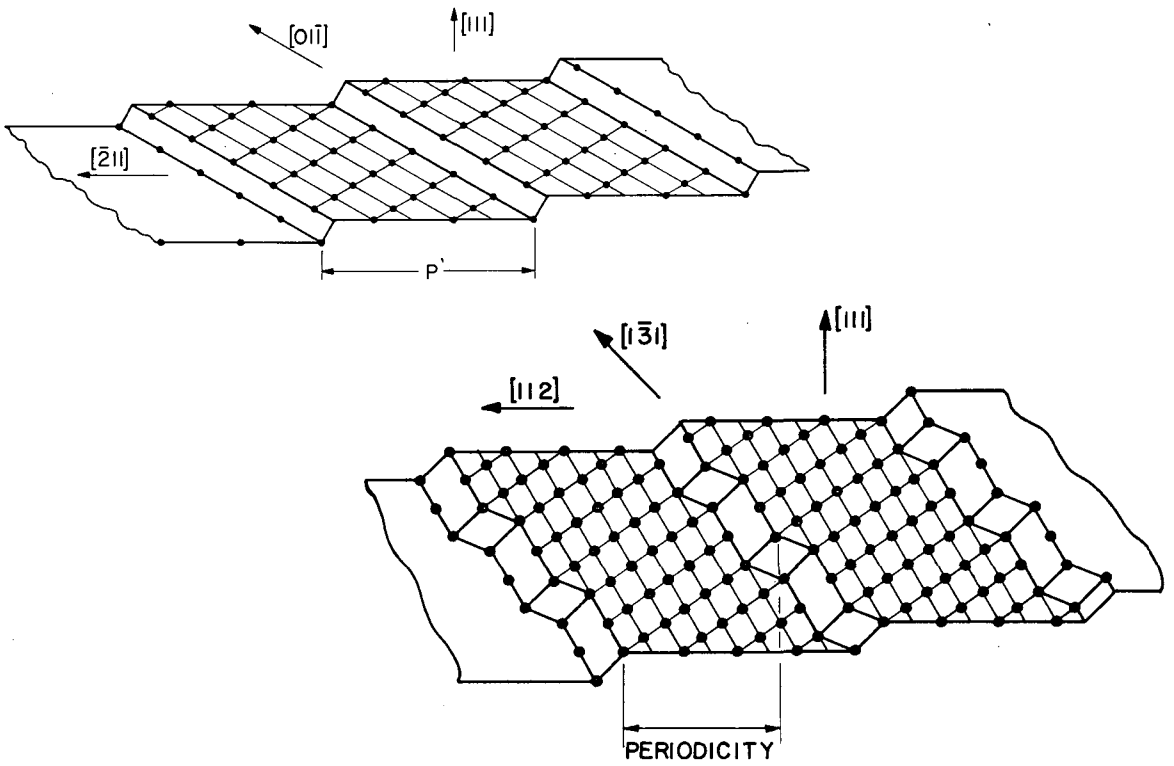


Fig. 4

COMPOSITION OF ALLOY SURFACES AS STUDIED BY AUGER ELECTRON SPECTROSCOPY

Principal Investigator: Gabor A. Somorjai

One essential piece of information in studying the behavior of a surface is its chemical composition. Minute concentrations of impurities or changes in stoichiometry can markedly modify the chemical or electronic surface properties.

Auger electron spectroscopy permits us to perform nondestructive surface chemical analysis and to detect changes in surface composition that involve as little as 1% of the surface atoms. This type of spectroscopy has been particularly important in studies of alloy surfaces and in studies of the surface composition of multicomponent systems in general. Thermodynamic considerations would indicate that the chemical composition at the surface of an alloy should be different from its bulk composition. Auger electron spectroscopy has confirmed that the surface of an alloy is enriched in one or another of its components. Since the surface composition in the topmost layers determines the chemical behavior, a detailed study of the surface phase diagram, i.e., the surface composition as a function of bulk composition, is of great importance since it may permit us to adjust the surface composition to our needs. For example, alloys used to contain steam at high temperatures and pressures are resistant to corrosion because of the segregation at the surface of one of the components, aluminum, that forms an impervious passive oxide layer in the presence of steam. Alloys are also used in the chemical industry with

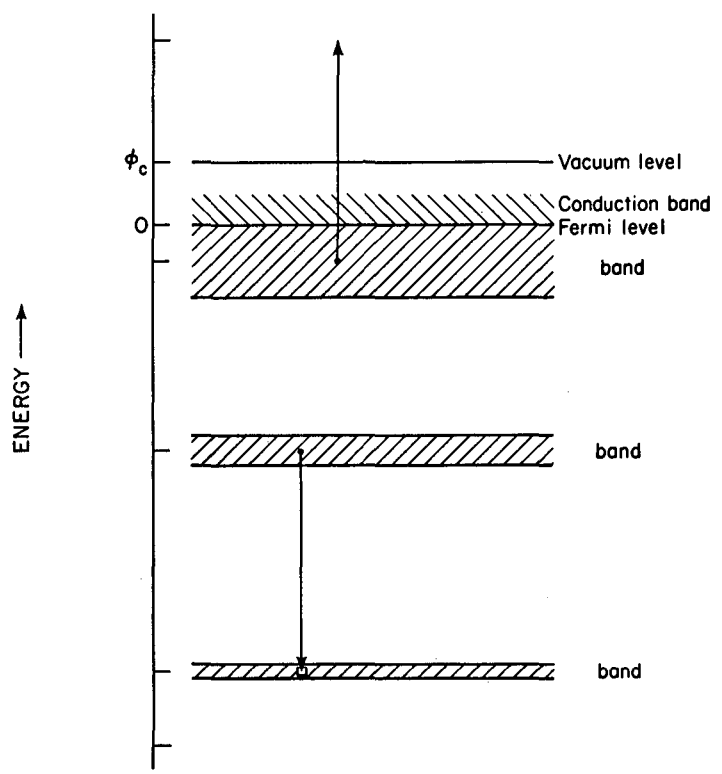


Fig. 1

increasing frequency as catalysts to carry out selective chemical reactions. Research in this laboratory is directed toward understanding the thermodynamic laws that govern the surface composition of alloys and toward discovering the relationship between surface composition and reactivity in catalytic surface reactions.

The technique involves the collection and energy analysis of electrons that are backscattered from a surface and have suffered energy losses in the scattering process. A diagram of the Auger electron emission process is shown in Fig. 1. Incident electrons create a vacancy in one of the inner shells of the surface atoms. This electron vacancy is then filled by an electron from an outer shell. The energy released by this transition is transferred to another electron in one of the electronic levels and that electron is then ejected. This is called the Auger electron emission process. Energy analysis of the emitted electrons will give differences in biding energy between electronic bands participating in the Auger process that are characteristic of a given element. Since most of the Auger electrons of lower energy can be reemitted only from the proximity of the surface (the top two or three layers), the Auger spectrum essentially depicts the surface composition. A typical Auger spectrum from a contaminated metal surface is shown in Fig. 2. The energy at which a peak occurs identifies the surface species, e.g., carbon. The height of the peak determines the surface concentration.

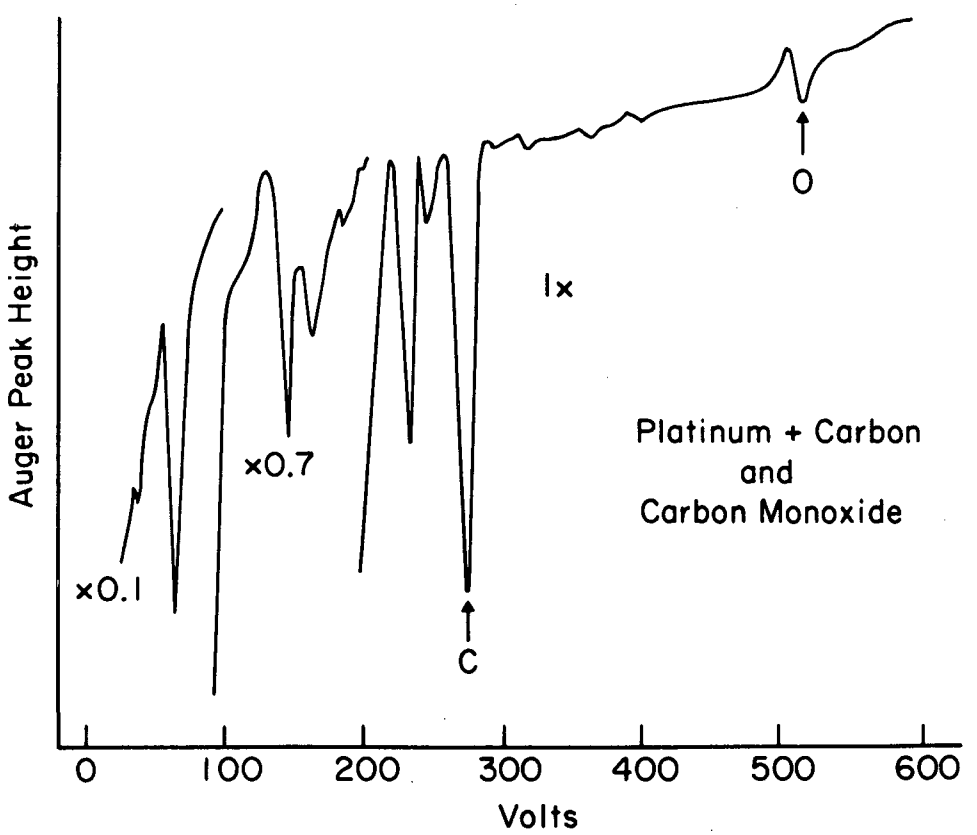


Fig. 2

HOW IS ENERGY DISTRIBUTED IN SURFACE REACTIONS? THE MOLECULAR BEAM-SURFACE INTERACTION

Principal Investigators: Gabor A. Somorjai and Yuan T. Lee

One of the important questions we must answer, in order to unravel the nature of surface reactions, is how the energy partitions in a chemical reaction between the reactants, product molecules, and surface atoms. Also it is useful to know the necessary minimum residence time of molecules on the surface for the chemical reaction to take place. To answer these questions we are studying the interaction of well-defined beams of molecules with crystals surfaces. The scheme of the beam-scattering experiment is shown in Fig. 1. A beam of molecules impinges on the surface and the scattered product molecules are detected as a function of angle (angular distribution) by a rotatable mass spectrometer detector. By chopping the incident or scattered beams periodically the flight time of the molecules can be determined. This experimental information yields the surface residence time of the impinging molecules before reemission to the gas phase, and the velocity and momentum of the incident molecules and of the scattered products. The surface structure and composition of the crystal surfaces are also determined, by simultaneously utilizing low-energy electron diffraction and Auger electron spectroscopy.

By using this sensitive molecular-beam probe, we have determined that the amount and type of energy transfer between the incident beam and the surface depends very much on the surface structure and composition. Molecules scattered from clean ordered metal surfaces undergo little loss of their kinetic energy (velocity). If the surface is covered with a layer of adsorbed molecules (for example, CO) the

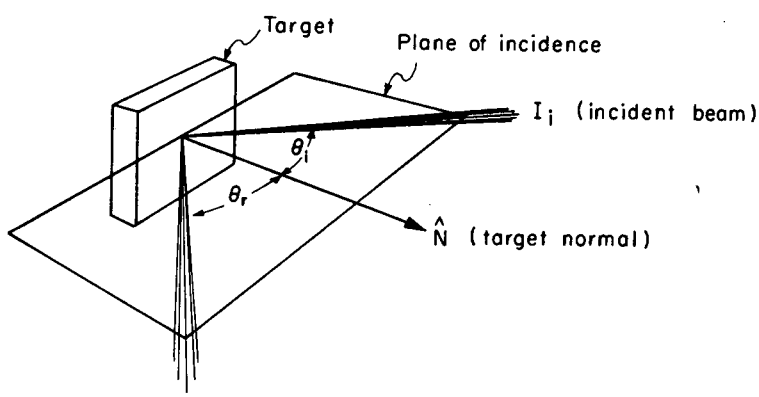


Fig. 1

impinging atoms or molecules lose all their kinetic energy to the surface and are trapped long enough that complete energy equilibirium occurs between the gas and the surface before re-emission of the molecule. We have also found that H_2 molecules dissociate only at the surface steps on platinum surfaces. In the absence of large concentrations of atomic steps the hydrogen molecules backscatter without dissociation, as indicated by the lack of HD product in studies of the H_2 - D_2 exchange reaction by the molecular-beam technique. This reaction can only occur if H_2 dissociates on the solid surface.

Studies are in progress to determine the partitioning of excess chemical energy that becomes available during the recombination of hydrogen atoms on crystal surfaces. The 103 kcal/mole energy that is liberated during the formation of the hydrogen molecule must be partitioned between the desorbing molecules and the surface atoms. Molecular-beam scattering will be able to determine the energy distribution in exothermic chemical reactions of different types.

CATALYSIS OF HYDROCARBON REACTIONS BY METAL SURFACES

Principal Investigator: Gabor A. Somorjai

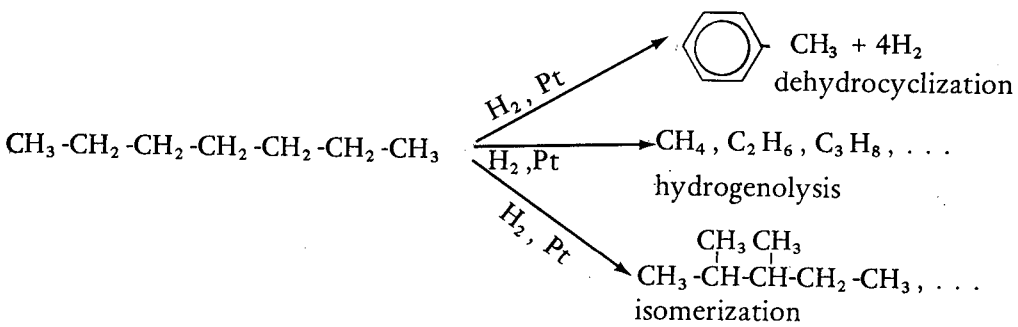
Heterogeneous catalysis occurs when a surface reduces the potential energy barrier in the path of reacting molecules to achieve thermodynamic equilibrium. For example, the reaction $H_2 + D_2 \rightarrow 2HD$ would not occur in the gas phase due to the large energy input (approximately 103 kcal) necessary to dissociate one of the diatomic molecules. However, this exchange reaction readily occurs at temperatures as low as 100°K on metal surfaces.

Heterogeneous catalysis can do much more than reduce the potential energy barrier in the path of the chemical reaction. A good catalyst can selectively catalyze one out of many competing and thermodynamically feasible reactions and aid in the formation of the desired products. For example, n-heptane may undergo several types of chemical reactions on a metal surface.

On platinum the complex dehydrocyclization reaction can occur at sufficiently high rates to produce aromatic molecules in large quantities. This is one reason for the widespread use of platinum as a "reforming" catalyst in the petroleum industry. The aromatic molecules have high "octane numbers" whereas the straight chain aliphatic molecules such as n-heptane have octane numbers near zero.

What is the atomic structure of the metal surface where catalysis takes place? Where are the surface sites at which the selective breaking of the H-H, C-H, and C-C bonds occurs? How does the complex rearrangement that accompanies dehydrocyclization take place on a metal surface? Answers to these fundamental problems are currently emerging from studies of catalytic reactions being carried out on single-crystal surfaces.

A typical metal surface is shown in Fig. 1. We can distinguish various surface sites where atoms have different numbers of nearest neighbors. There are atoms in steps and kinks in the steps. Atoms are present in large numbers in the well-ordered terraces where they are surrounded by the largest number of nearest neighbors. There are atoms, called adatoms, that diffuse along the terraces; adatoms have the smallest



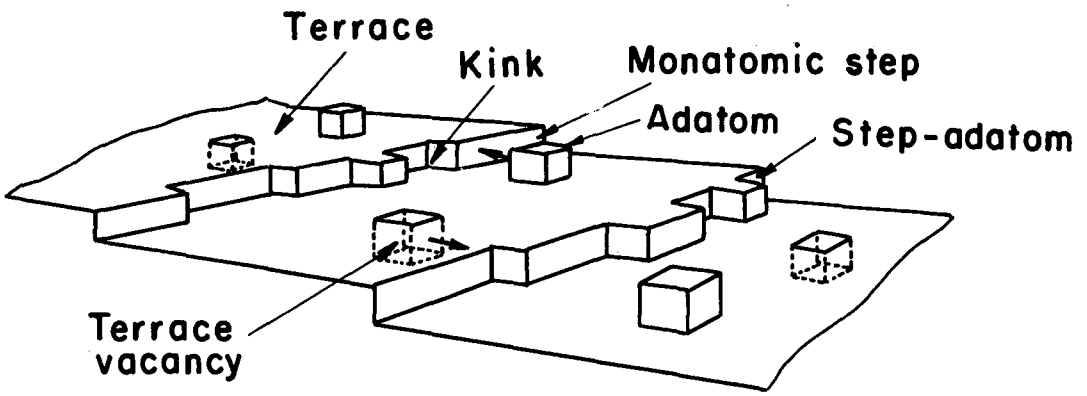


Fig. 1

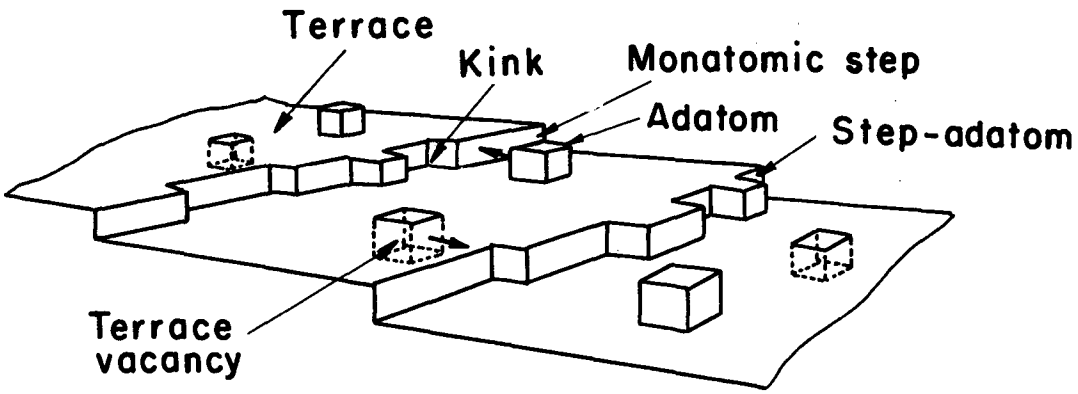
number of nearest neighbors. Atomic vacancies are present in the terraces. Experimental evidence for the presence of all of these different surface sites comes mostly from low-energy electron diffraction and field ion microscopy studies.

By using single-crystal surfaces, we can prepare atomic surface structures in such a way that a large concentration of the desired atomic steps or kinks is present. Surfaces having 20 to 30% of all atoms located in steps have been prepared. Conversely, surfaces with very low density of irregularities (steps, kinks) have also been prepared by cutting single crystals along surfaces of low Miller Index.

The relationship between the atomic structure and reactivity can be explored by studying the catalytic activity of these crystal surfaces that were prepared with well-defined atomic surface structure.

Our discussion will be restricted to platinum. It will serve as a model to introduce the atomic structure of the various types of surfaces that are important in catalysis and to describe the fundamental steps of important catalytic reactions.

Recent studies indicate the complex chemical surface reactions of low-reaction probability can readily be studied in our apparatus on one face of a crystal whose surface area is $\approx 1\ cm^2$. At low pressures (10^{-6} to 10^{-4} Torr) the reactant and product distributions are monitored by mass spectrometry and at high pressures (atmospheres) by gas chromatography. Catalytic reactions ranging from the exchange of $H_2 + D_2$ to form HD, to the dehydrogenation of cyclohexane, and the rearrangement of n-heptane have been studied in this way. The reaction probability of HD formation at low pressure on stepped surfaces was found to be on the order of 10^{-1}. On a crystal face without a large concentration of steps a reaction probability as low as 10^{-4} is hardly detectable. Atomic steps play a controlling role in breaking the H-H bond, the prerequisite to forming HD. Similarly, atomic steps are necessary to efficiently break C-H bonds that take place during the conversion of cyclohexane (C_6H_{12}) to benzene (C_6H_6). On platinum crystal surfaces that have large concentrations of kinks, efficient hydrogenolysis reactions occur that are the result of C-C bond-breaking processes. In studies of hydrocarbon reactions on platinum crystal surfaces where several reaction paths are possible,



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microstructures on the surfaces have been identified where C-C bond-breaking also occurs in addition to C-H and H-H bond-breaking processes. At other microstructures only C-H and H-H bond-breaking processes predominate. It appears that surface irregularities or various surface sites with different coordination numbers have different and distinct chemical activity. Apparently transition metals, with unfilled d-orbitals and high electron density of states, are the group exhibiting multifunctional reactivity behavior controlled by detailed atomic structure of the heterogeneous surface. By preparing transition metal surfaces with controlled concentration and configurations of atomic steps and kinds, the reaction rate as well as the reaction specificity may be controlled.

n-Heptane may react along several reaction paths on platinum surfaces as shown above, and these various reactions have been studied as a function of the atomic surface structure of platinum. We find that shortly after the reaction begins the surface becomes covered with an overlayer of carbonaceous deposit that is either disordered or ordered, depending on the conditions of the experiment and on the platinum surface structure. Whether the reaction is carried out at low or high pressure, the catalyst surface is largely covered by the carbonaceous overlayer. The model of the platinum surface that yields steady-state rates and product distributions during the catalysis of hydrocarbon reaction is shown in Fig. 2. Irregular terraces of platinum atoms perform the various C-C,

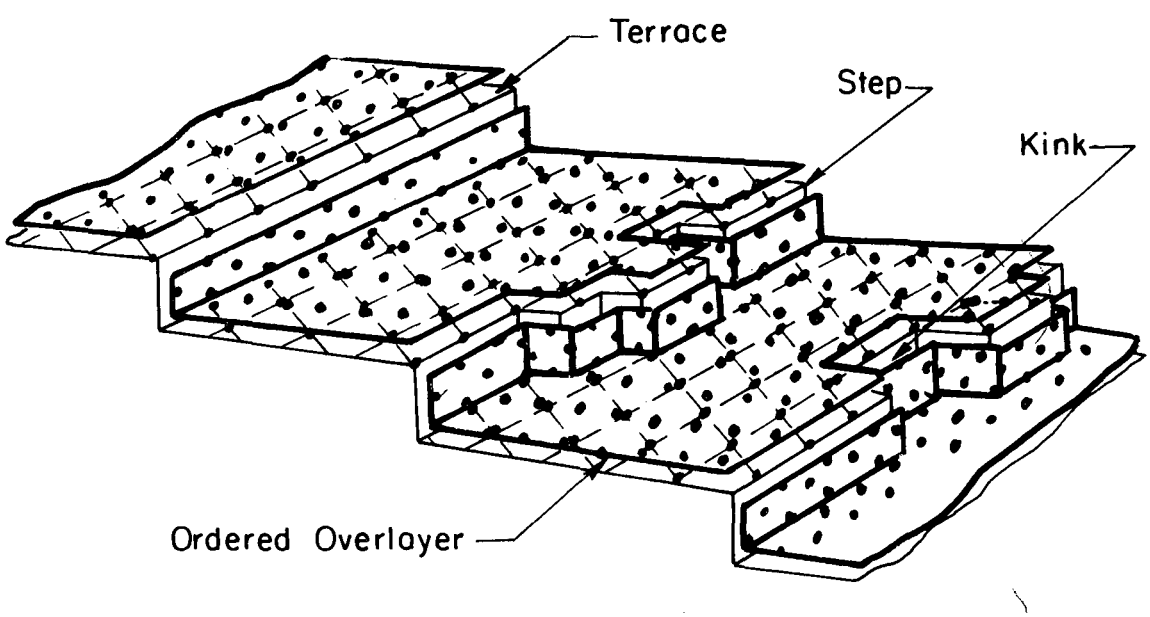


Fig. 2

C-H, and H-H bond-breaking functions and perhaps some of the molecular rearrangements. Then the species breaks away from the metal atoms, diffuses onto the terrace that is covered with the carbonaceous overlayer where further rearrangements may occur, and desorbs the product molecule.

Other important catalytic reactions are being studied, such as the nitrogen fixation requiring N≡N bond-breaking or the reaction of CO with H_2 necessitating C = O and H-H bond-breaking. Similar studies on other metal surfaces will lead to an understanding of the elementary steps of heterogeneous catalysis on a molecular level: adsorption, surface diffusion, bond-breaking, rearrangement, and desorption. The understanding of catalytic surface reactions on an atomic scale, uncovering the relationship between atomic structure and reactivity, is the foundation of catalysis science that attempts to develop more selective, more poison-resistant, and more efficient catalysts.

PRODUCTION OF SYNTHETIC FUELS BY CATALYZED REACTIONS OF CARBON MONOXIDE (CO) AND HYDROGEN (H_2) FOLLOWING COAL GASIFICATION

Principal Investigator: Gabor A. Somorjai

The conversions of coal to synthetic fuel has become a problem of major importance in the United States because of a) the rising cost of crude oil and b) the abundance of coal in this country. One route involves the gasification of coal in three steps. First a mixture of H_2 and CO is produced by the reaction of water vapor with hot coal ($C + H_2O = CO + H_2$). Then the mixture is enriched in H_2 by the reaction ($CO + H_2O = CO_2 + H_2$). Finally the CO-H_2 mixture is reacted over a suitable catalytic surface to produce a mixture of hydrocarbons. On certain catalyst surfaces, on nickel for example, only methane (CH_4) forms under appropriate experimental conditions. On other catalyst surfaces (on cobalt, iron, rhodium, and thorium oxide for example) a mixture of longer chain hydrocarbons is produced. This latter process is called the Fischer-Tropsch reaction and was used in Germany during World War II with a cobalt catalyst to produce low-octane synthetic fuels.

If we are to produce high-quality synthetic fuels, it is essential to understand the mechanism of this reaction on the molecular level. By controlling the catalytic surface structure and composition, one, or only a few, desired product molecules are synthesized. This objective is pursued through physical characterization of the catalyst, identification of the structure and quantity of adsorbed species, and measurements of the reaction kinetics as a function of surface composition and surface structure.

The reactions of CO and H_2 are commonly divided into two classes: those leading to methane

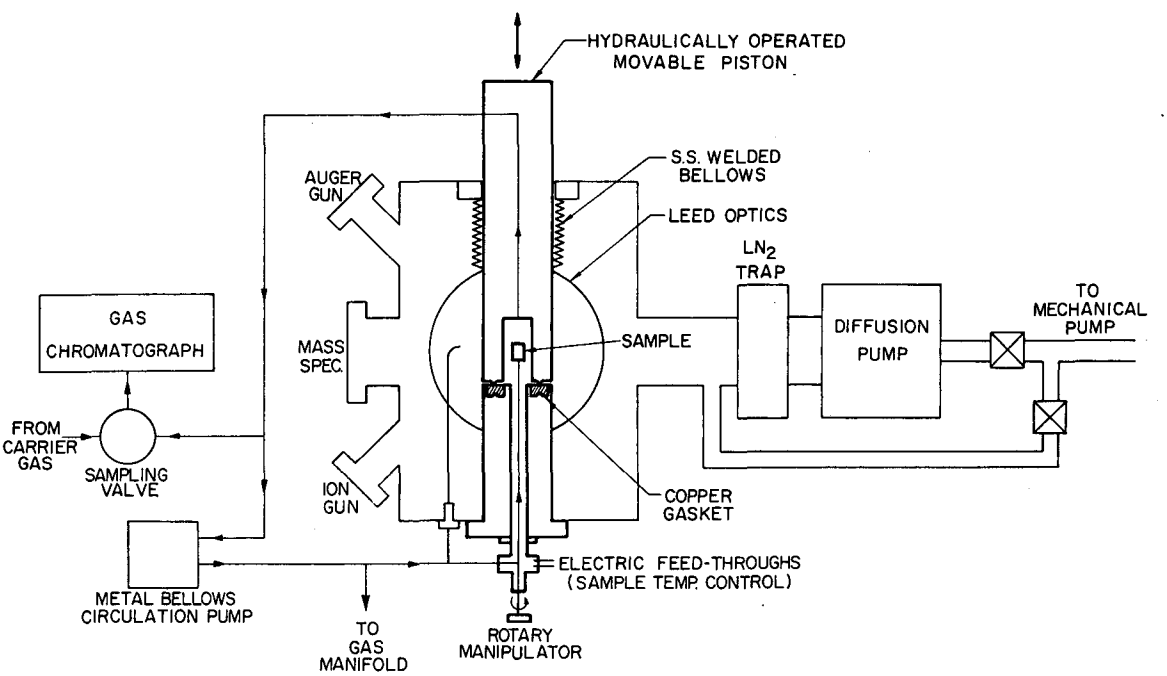


Fig. 1

formation (or perhaps methanol) and those that yield molecules in which there are several carbon-carbon bonds (longer chain hydrocarbons). The latter requires the "insertion" of several carbon species into the molecular chain in addition to hydrogenation, while the former involves only hydrogenation. The rates of both classes of reactions are slow and are controlled by specific surface bond-breaking and bond-forming processes in all conditions of the experiment.

We have studied the formation of methane on rhodium crystal surfaces by using a high pressure-low pressure apparatus that operates in the 10^{-8} Torr 100 atm range that is shown in Fig. 1. The apparatus incorporates all of the surface analysis features (LEED, AES, mass spectrometry) and permits analysis of the catalyst surface before and after the high pressure reaction without removing the sample from the reaction chamber.

Our studies indicate that CO dissociates on the rhodium surface. Carbon is retained, bound to the metal on and below the surface, while oxygen atoms are removed efficiently by excess H_2 or CO as water or carbon dioxide under the reaction conditions. The rate of the methane formation is controlled by the rate of hydrogenation of the carbon at the rhodium surface. The rhodium-carbon surface complex appears to be very active in this reaction. We found that CO_2, when substituted for CO, forms methane significantly faster than carbon monoxide.

We are studying the reaction of CO with H_2 on various well-characterized metal surfaces (rhodium, iron, thorium oxide, and cobalt) in an attempt to isolate the various insertion reaction paths that are responsible for the formation of alcohols, and saturated and unsaturated hydrocarbon molecules.

LIGHT-ASSISTED SURFACE REACTIONS. THE PRODUCTION OF HYDROGEN AND OXYGEN BY WATER DISSOCIATION ON SEMICONDUCTOR SURFACES

Principal Investigator: Gabor A. Somorjai

In this project we explore the surface properties of materials that carry out photon-assisted chemical reactions. These are semiconductors with band gaps of ~2 eV or greater. Among them, TiO_2 and GaP appear to be very promising for the photon-assisted conversion of water to form H_2 and O_2. An electrochemical cell using TiO_2 as the anode and p-type GaP as the cathode was shown to be capable of the electrolysis of water with no external voltage required when the electrodes were irradiated.

Reactions that are catalyzed by surfaces must be thermodynamically feasible. Yet many reactions of great importance like the reactions of H_2O and CO_2 to produce hydrocarbons and oxygen (photosynthesis) or the dissociation of water are not thermodynamically feasible. In this circumstance, light that creates photoelectrons of reasonable lifetimes at the solid surface is used to assist the chemical reaction. The purpose of our studies is to understand the role of the photoelectron in the reactions of water and carbon dioxide. Using this knowledge we should be able to develop materials with suitable surface structure and composition to optimize the photon-assisted reaction rates and product distributions. If energy can be provided by sunlight and efficiently utilized in the course of these reactions, hydrogen and hydrocarbons may be produced.

Well-characterized titanium oxide crystals are being used in our studies to explore the mechanism of adsorption of oxygen, hydrogen, and water and the light-assisted dissociation of water on the various crystal surfaces of this material. It is hoped that light-assisted catalytic reactions will play an important role in synthetic fuel production.

STUDIES OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF ADSORBED MOLECULES BY SURFACE REFLECTANCE AND EMISSION SPECTROSCOPY

Principal Investigator: Charles B. Harris

The question of how the metal surface alters molecular and electronic structures of molecules upon adsorption is one of the most important in modern surface chemistry. To answer this question, we are developing reflectance and emission spectroscopy from aromatic hydrocarbon monolayers absorbed on Ni(111), W(111), Pt(111), and high Miller-index faces.

The arrangement of the reflectance experiments is illustrated in Fig. 1. A laser (or any other source) impinges on the surface at near-grazing incidence and its electric field is vector-parallel to the plane of incidence. The incident and reflected intensities are measured as a function of wavelength. From this information we can obtain both the frequency and width of an infrared or electronic transition of a molecule when it is in contact with a surface. By increasing the thickness of the overlayer, we can obtain the same information when the molecule is in the bulk state, and hence extract the energy shift in the vibrational and electronic states induced by the surface. From this information we can derive a detailed picture of the molecular and electronic structure of these molecules on various surfaces. It is also possible to obtain the orientation of the molecule relative to the surface plane by analyzing the data. The surface structure, the absorbate structure, and the composition are analyzed simultaneously by low-energy electron diffraction, plus photoelectron spectroscopy and/or Auger electron spectroscopy. Studies are also in progress to analyze the emission from electronically excited states of aromatic hydrocarbons in the visible and UV ranges. This information will provide us insight into the strengh of bindings of the adsorbed species to the surface, and the redistribution of energy due to adsorption and bonding to the surface.

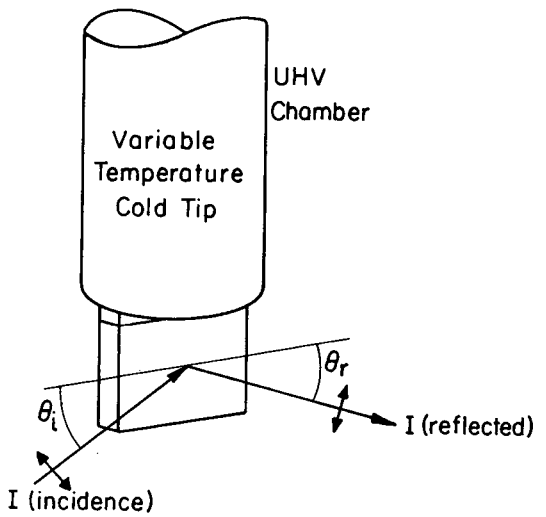


Fig. 1

CHEMISORPTION BONDING OF MOLECULES TO SURFACES FROM PHOTOEMISSION SPECTROSCOPY

Principal Investigator: David A. Shirley

The first step in heterogeneous catalysis is the formation of a chemisorption bond between a reactant atom or molecule and the catalytic substrate. This prepares the reactant by lowering the activation energy of the subsequent reaction. Hence any postulated mechanism for a catalyzed reaction must begin with a statement about the nature of the interaction between the adsorbed species and the substrate.

Until recently there existed no spectroscopic technique for determining the electronic structure of adsorbate-substrate systems. With the advent of ultrahigh vacuum techniques, coupled with photoelectron spectroscopy, it is now possible to observe individual electronic orbitals of adsorbates <u>in situ</u>. A system under intensive recent study is CO adsorbed on Pt or Ni crystals. This system is of considerable catalytic interest because CO/Pt is used in Fischer-Tropsch syntheses. Let us use it as an example.

Photoemission studies of CO/Pt in this laboratory have demonstrated a very high spectral sensitivity to the 4σ and $(5\sigma + 1\pi)$ peaks of CO at photon energies of 150 eV, available at the Stanford electron storage ring (Fig.1). Also shown is a decrease in substrate (platinum 5d) peak intensity near the Fermi energy. This shows electron transfer from platinum t_{2g} orbitals into the $1\pi^*$ orbitals of CO.

The developing technique of angle-resolved photoemission (ARP) affords the possibility of obtaining still more information about adsorbates. The angular distribution of photoelectrons in each

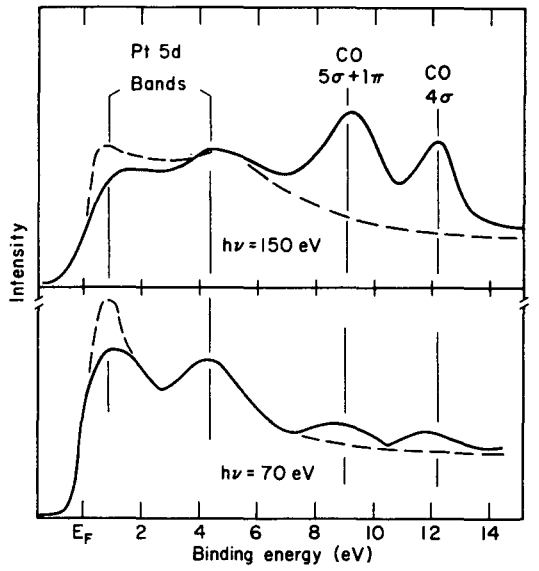


Fig. 1

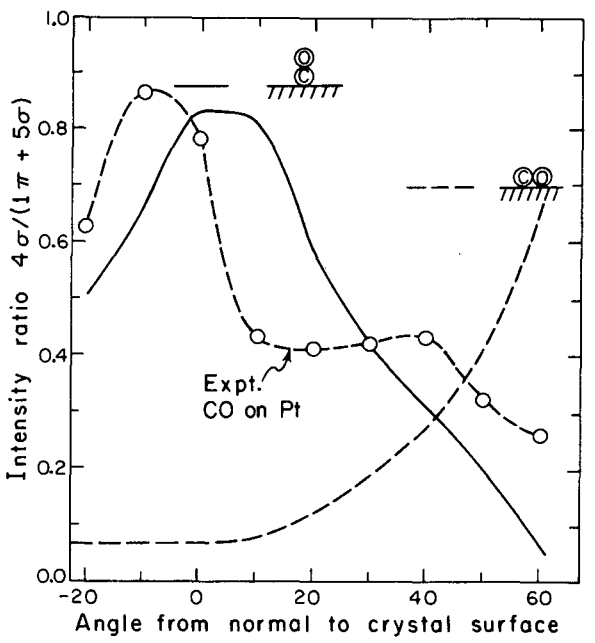


Fig. 2

orbital peak maps the orientation of that orbital, hence of the adsorbate. In this laboratory ARP has been used to show that CO stands up when chemisorbed on a Pt(111) or Ni(111) surface (Fig.2). Further studies have shown that the 5σ and 1π orbital energies are reversed relative to the gas phase. Thus we now have a fairly complete picture of the electronic orbital structure in the CO/Pt system (Fig. 3).

Carbon monoxide bonds to platinum "standing up", by formation of a C-Pt bond. The carbon lone pair (5σ) electrons are polarized toward Pt, raising the 5σ binding energy. Platinum 5d electrons in the t_{2g} orbital near the Fermi energy "back-bond" into the CO π* orbitals. All of this information was derived from photoemission data.

The CO/Pt case is only one example of catalytic systems that can be studied by angle-resolved photoemission. Other systems are under continuing study in this laboratory.

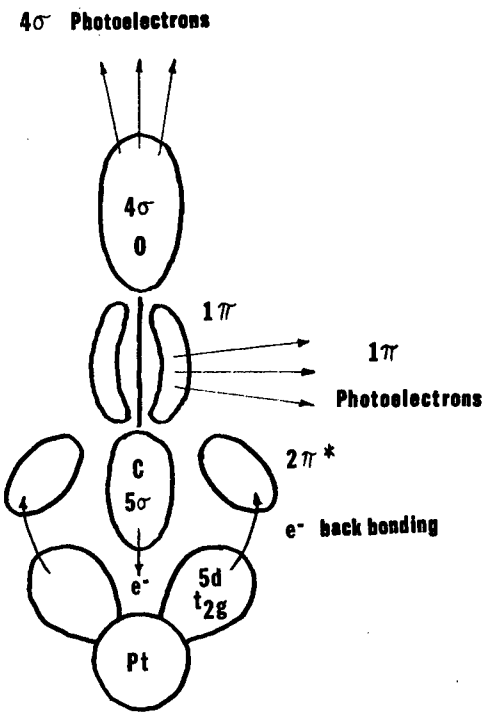


Fig. 3

PHOTOEMISSION STUDIES OF ELECTRON STATES AT CLEAN SURFACES

Principal Investigator: David A. Shirley

Photoelectron spectroscopy is a particularly powerful tool for studying electronic states in solids. In the past, photoelectron spectra have been interpreted almost exclusively in terms of bulk band structure effects. More recently, however, it has become clear that photoemission spectra show both surface and bulk features. The study of surface-derived effects is greatly aided by the availability of synchrotron radiation. As is seen from Fig. 1, the photoelectron mean free path in most materials is shortest at a kinetic energy around 100 eV. In this energy range the photocurrent therefore arises largely from the surface layer of the material. A special advantage of using synchrotron radiation rather than laboratory photon sources (see Fig. 1) is that one can tune into the surface-sensitive energy range and thus enhance surface over bulk effects.

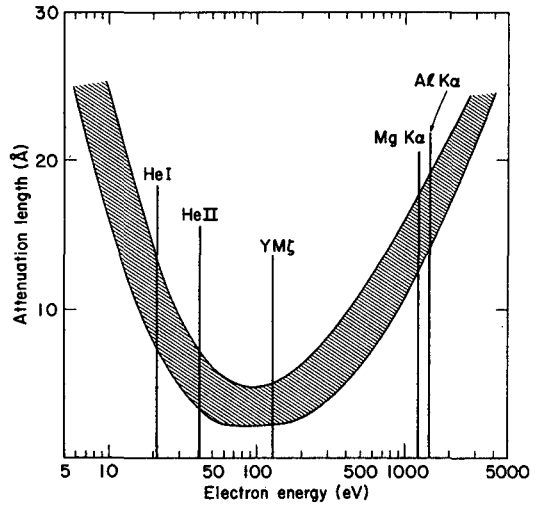


Fig. 1

In the following we shall discuss two examples of such studies carried out at the Stanford Synchrotron Radiation Project (SSRP) on the storage ring SPEAR. The first example demonstrates that the bulk band structure is modified at the surface. This result is intuitively expected and has been predicted theoretically for several years. The most interesting result of such calculations is the prediction of a narrowing of the d-band density of states near the surface. In a simple physical picture such a behavior is expected because the reason for broadening atomic levels into solid-state bands is partly removed at the surface. This effect is demonstrated experimentally in Fig. 2 by using angle-resolved photoemission from the (001) and

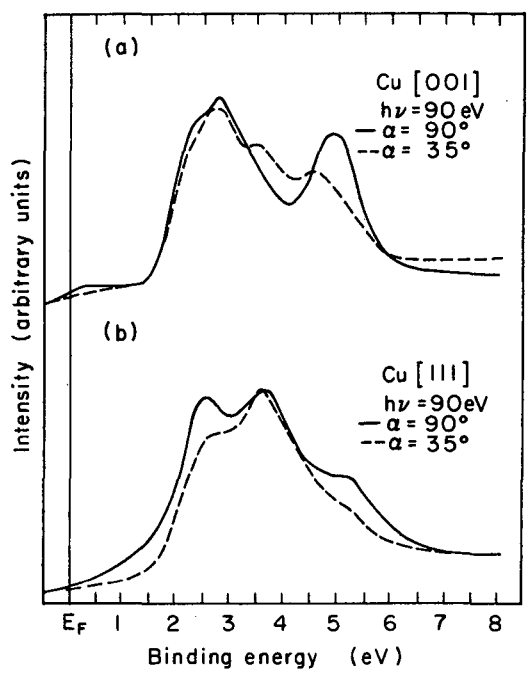


Fig. 2

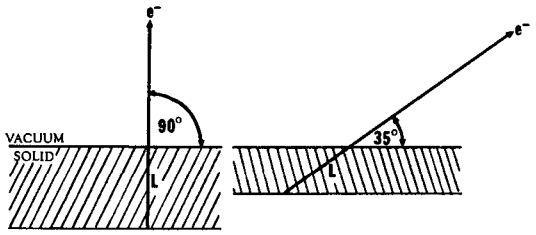


Fig. 3

(111) faces of a Cu single crystal. As shown in Fig. 2 the experimental spectra for photoemission along both the [001] and [111] directions become narrower when the electron take-off angle from the surface is decreased from 90° to 35°. The narrowing of the d-band width is accompanied by an increase of the central peak (~3.7 eV BE), which coincides with the center of gravity of the d-band. As seen from Fig. 3, the above change in angle corresponds to a decrease in effective sampling depth inside the crystal by a factor of approximately 2. In the low take-off angle case ($\alpha = 35°$) the surface-derived contribution to the spectrum is considerably enhanced. The fact that the escape depth is already short at $h\nu = 90$ eV (see Fig. 1) makes us believe that we are largely sampling the outermost layer of the crystal in the low take-off angle case.

The influence of the surface on the photoemission spectrum is also clearly revealed by a comparative study of a Pt(111) and a Pt(S) - [3(111)×(100)] crystal. Figure 4 shows the microscopic atomic positions in the surface of the stepped Pt crystal. The surface consists of a sequence of (111) and (100) planes. The macroscopic crystal face is the (211) plane. In Figs. 5a and b we compare angle-resolved photoemission spectra that were recorded along the [111] direction of a Pt(111) and a Pt(S) - [3(111)×(100)] crystal. The observed differences between corresponding spectra in columns a and b of Fig. 5 can only

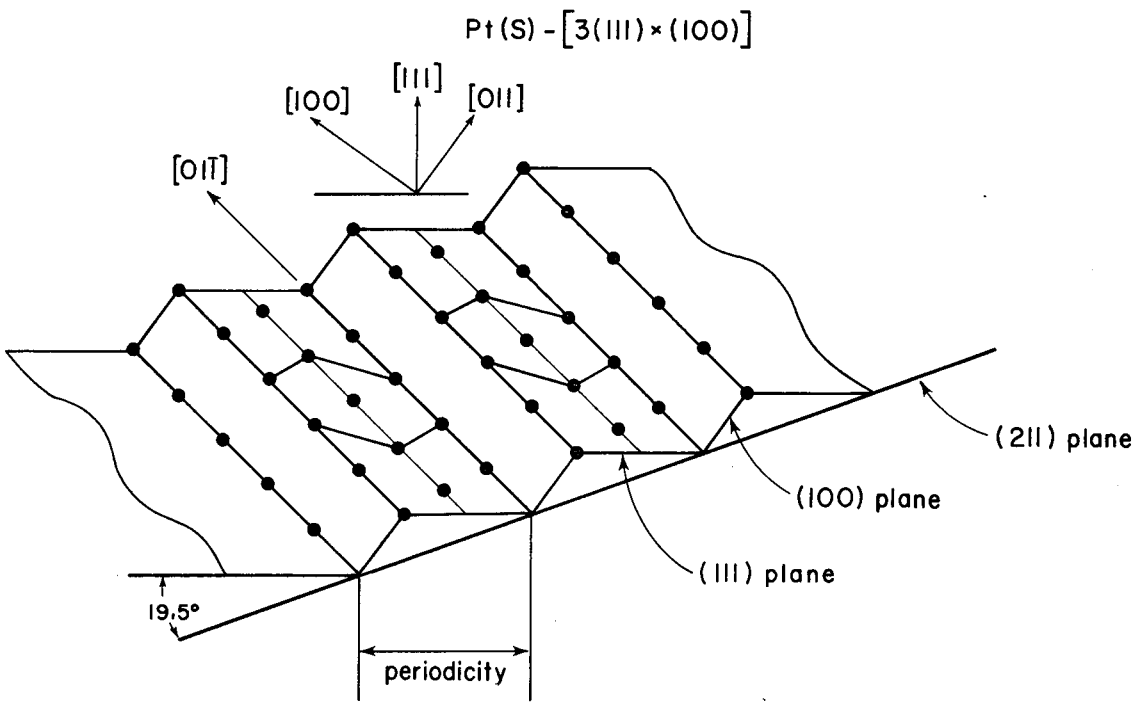


Fig. 4

arise from surface effects since both spectra were recorded along the same (i.e., the [111]) bulk direction. Figures 5c and d exhibit similar strong differences between spectra taken along another arbitrary photoemission direction. In this case the detector was oriented 30° of the [111] toward the [110] direction (compare with Fig.4). We attribute the observed differences between the spectra in Figs. 5a and b and Figs. 5c and d, respectively, to a different local density of states at the surface for a flat Pt(111) and stepped Pt(111)×(100) surface. This interpretation is confirmed by the fact that the most striking difference between corresponding spectra in Fig. 5 are observed in the surface-sensitive region around 100 eV, while the differences are smallest at the lowest (40 eV) and highest (150 eV) energies.

The stepped surface structure is expected to modify the bulk bands extending to a flat surface. Also, the stepped structure gives rise to new surface states whose energies correspond to a band gap in the bulk. A detailed understanding of these electron states at clean surfaces is essential for the understanding of reaction mechanisms (chemisorption, catalysis) between such surfaces and gases.

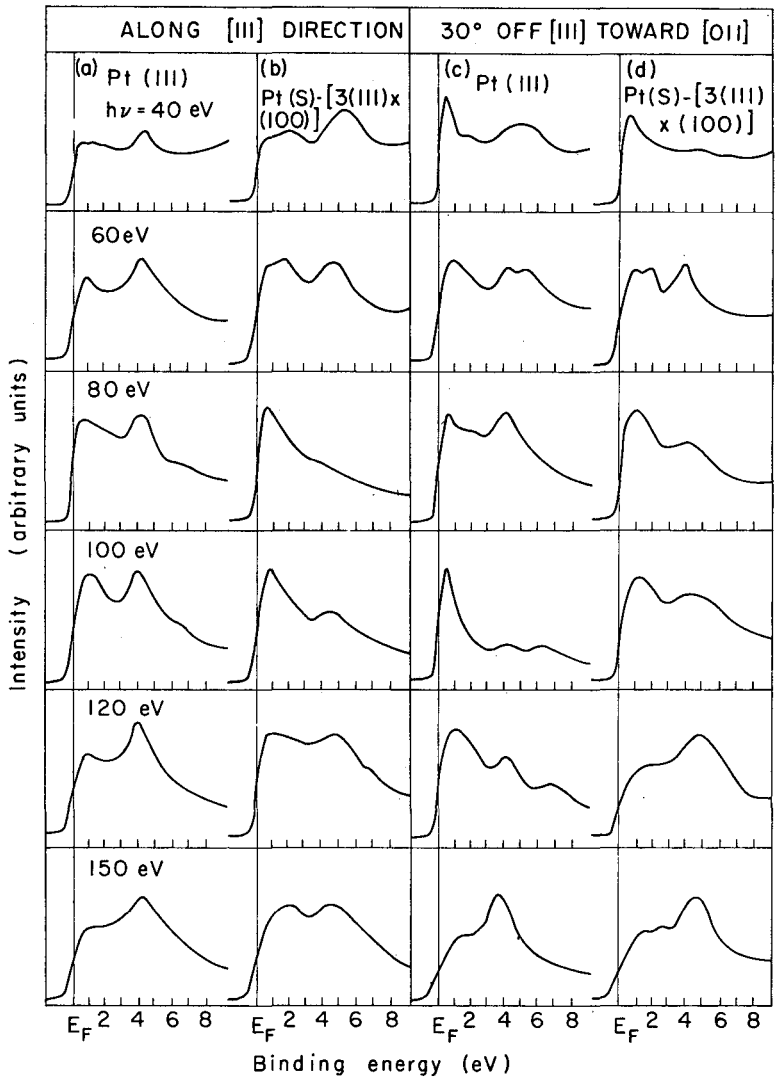


Fig. 5

STUDIES OF MOLECULAR ADSORPTION AND DESORPTION

Principal Investigator: Alexis T. Bell

The adsorption of reactants and the desorption of metal products are important steps in the progress of a reaction occurring on the surface of a catalyst, and in some instances, control the rate of reaction. As a result it is essential to measure the rates of adsorption and desorption of individual reaction components and to characterize the strength of catalyst-adsorbate interactions.

To study the kinetic and energetics of adsorption and desorption we have constructed an apparatus consisting of a recording microbalance and a vacuum manifold. This system operates at pressures between 10^{-5} Torr and 1 atm. The microbalance has a sensitivity of 0.1 μg, which makes it possible to detect fractional monolayer coverages of light gases such as H_2.

Currently, studies are being carried out to characterize H_2, CO, and NO chemisorption on supported noble metal catalysts. Of particular interest is the nature of bonding and the binding energies of the adsorbed molecules. The latter can be determined from thermal desorption spectra. Such spectra are obtained by measuring the rate of desorption from a catalyst when a sharp temperature ramp is imposed on the sample. Figure 1 illustrates a desorption spectrum for H_2 on silica-supported Ru. The peaks indicate that there are multiple forms of adsorbed H_2.

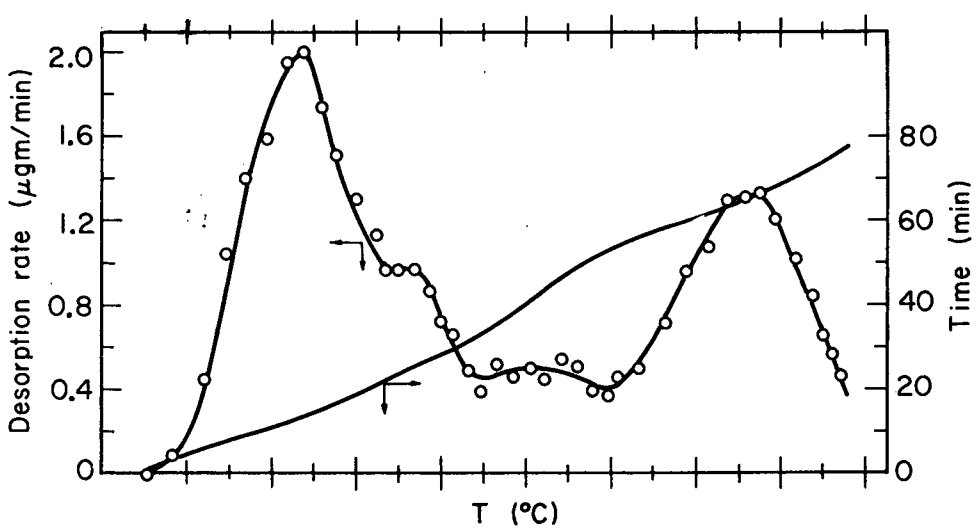


Fig. 1. Thermal Desorption Spectrum of Hydrogen
-o- Desorption Rate vs. Temperature
—— Temperature Ramp, Time vs. Temperature

STUDIES OF CATALYTIC REACTION MECHANISMS BY INFRARED SPECTROSCOPY AND KINETIC ANALYSIS

Principal Investigator: Alexis T. Bell

As the field of catalysis develops, it is becoming increasingly evident that in order to identify the elementary processes associated with catalyzed reactions, rate measurements must be supplemented by knowledge of the species adsorbed on the catalyst surface. When dealing with supported catalysts, a technique well-suited for this purpose is infrared spectroscopy. From such spectra the surface structures formed by an adsorbed gas can be deduced. If the spectra are recorded under reaction conditions, then surface structures can be observed for reactants, products, and intermediates.

Infrared spectroscopy is being combined with measurements of reaction rates and adsorption rates to study the mechanisms of a number of catalyzed reactions. All of the catalysts used for this work are supported on finely divided silica or alumina. Prior to their use in catalyzing a reaction, the catalysts are characterized to determine their bulk elemental composition, the size of the catalyst crystallites, and the surface area of both the support and the catalyst.

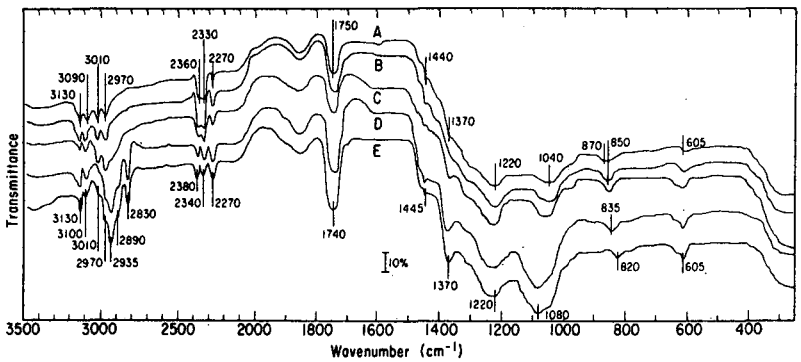
Reaction-rate and infrared spectra of adsorbed species are obtained by using a specially designed apparatus. The central component of this apparatus is a reactor that doubles as an infrared cell and is located in the sample compartment of an infrared spectrometer. A thin disc of supported catalyst is placed inside the reactor together with a disc of the support material. By aligning the catalyst disc with the sample beam of the spectrometer, and the support disc with the reference beam, spectra can be recorded of adsorbed species present on the catalyst surface. These spectra are not obscured by gas phase or support absorptions, due to the cancellation of these adsorptions. The balance of the apparatus is used to supply reactants to the reactor. The products of reaction are analyzed by gas chromatography.

The combined techniques of infrared spectroscopy and reaction-rate analysis have been used to study the reduction of NO by CO over CuO and Pt and the oxidation of C_2H_4 over Ag. An example of the spectra obtained under reaction conditions, taken from the latter study, is shown in Fig. 1. Also shown in this figure are the spectra for some pure components adsorbed on the same catalyst sample. Such spectra, together with information taken from the literature, have been used to make the structural assignments shown in Table 1.

In current studies we are continuing to investigate the reduction of NO over transition-metal catalysts. The objectives are to identify the cause of the observed activity and the selectivity patterns for such metals. Among the important problems being investigated is the mechanism by which ammonia is produced. This product is highly undesirable, and its formation must be surpressed if NO_x convertors are to be developed for use in automobiles.

Most recently a series of studies have been initiated relating to Fischer-Tropsch synthesis. Here the objectives are to determine the reaction intermediates that can be identified and the role of these intermediates in di-

recting product distribution.
Among the catalysts being studied
are Ru, Rh, and Fe.

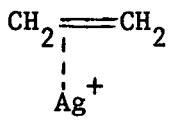
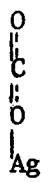
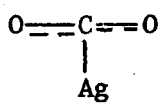
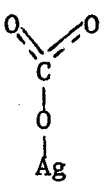
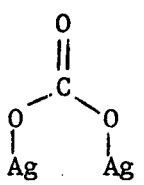
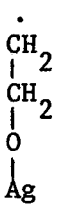
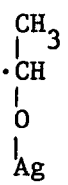


Spectrum	A	B	C	D	E
Time (hr)	1	5	9	14	18
P_{O_2} (atm)	0.375	0.313	0.280	0.259	0.244
$P_{C_2H_4}$ (atm)	0.170	0.136	0.116	0.103	0.096
P_{CO_2} (atm)	0.010	0.042	0.060	0.073	0.077
P_{H_2O} (atm)	0.010	0.042	0.060	0.073	0.077
$P_{C_2H_4O}$ (atm)	0.004	0.020	0.030	0.038	0.040
$r_{C_2H_4O}$ $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	147	105	71	33	17
r_{CO_2} $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	332	196	119	57	21
$S_{C_2H_4O}$ (%)	47	52	55	54	62

Fig. 1. Comparison of the spectra for adsorbed ethylene and ethylene oxide with a spectrum taken under reaction conditions: T = 220°C.

Table 1

Assignment of Infrared Bands to Surface Structures

$\nu(cm^{-1})$	Structure	
3130 3090 3020 2980		(I)
2270		(II)
2350		(III)
1365 1230 1035 810 605	 (IV) and 	(V)
2970 2920 2890 2920 1080 860	 (VI) and 	(VII)

PHYSICAL PROPERTIES OF SMALL METAL CLUSTERS

Principal Investigator: John S. Winn

Clusters of metal atoms, ranging in size from two to ten atoms or more, constitute a molecular family about which very little is known. The role of such clusters in physical phenomena such as nucleation, alloy formation, catalysis, and thin film properties is understood from a macroscopic viewpoint only. Thermodynamic quantities extrapolated from bulk or surface properties are the main source of our current knowledge. As evidence has grown regarding the specific chemical activity of small metal clusters, particularly in regards to catalytic activity, the need for microscopic measurements of the physical properties of these clusters has become more urgent.

The types of measurements needed are of the most fundamental variety: Ionization potentials, electron affinities, bond energies, dipole moments, and magnetic properties are among the important physical parameters of small metal clusters on which scant information is available. Spectroscopic information (geometries, force constants, electronic state designations, precise dipole moments) are of importance to the understanding of chemical properites of these species. The advent of new molecular-beam techniques promises methods of measuring many of these properties for a wide range of metals and cluster sizes.

In our laboratory, we have a versatile molecular-beam spectrometer, which can produce metal beams of varying cluster-size distributions and can subject these beams to many of the measurements described above. In Fig. 1, we show a block diagram of the spectrometer. The various components are modular and can be removed or disabled as needed for a given

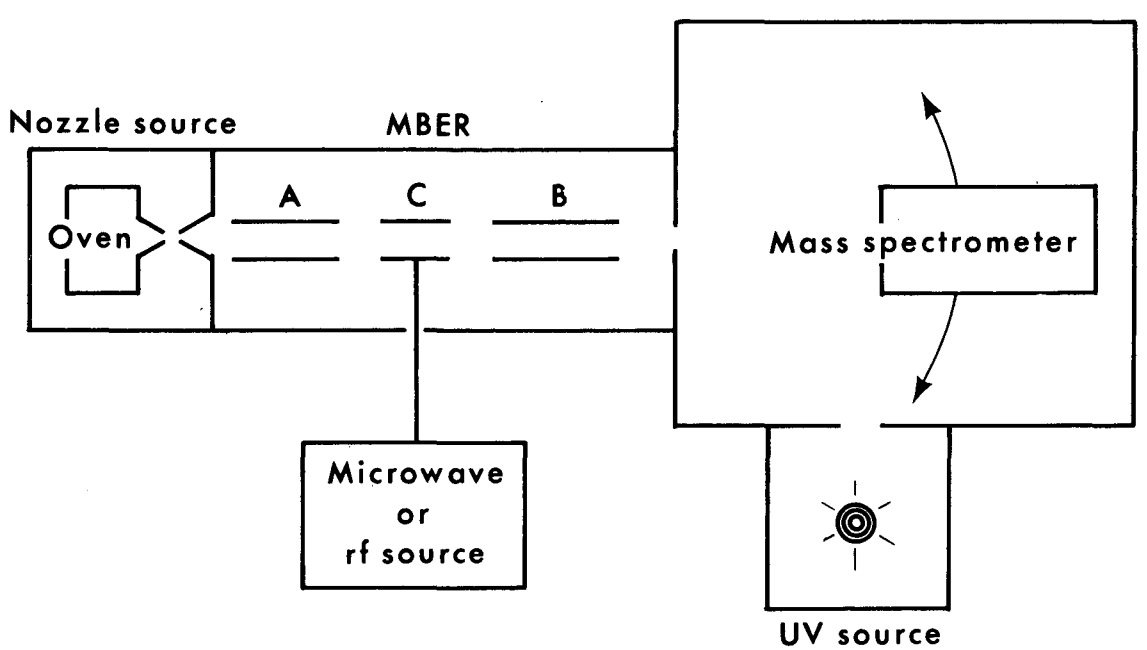


Fig. 1

measurement. At the heart of the apparatus is the high-pressure supersonic nozzle source. A supersonic expansion of metal vapor, usually in the presence of a carrier gas such as argon or helium, produces a non-equilibrium distribution of metal clusters in the resultant beam. The composition of the beam is monitored by a mass spectrometer system which is highly specialized. The ionizer can be operated to produce positive ions from electron bombardment in the usual way or to produce negative ions from dissociative electron capture onto a cluster. In addition, the beam can be photoionized by a dispersed UV light source, which can serve as the source of ionization. Mass analysis is performed in a quadrupole mass filter, and selected ions are detected with a particle multiplier. The entire mass spectrometer assembly can be rotated inside the main vacuum chamber for the study of angular-dependent processes such as photodissociation or various beam deflection phenomena.

The components of a molecular-beam electric resonance spectrometer are housed in the chamber labeled MBER. These components consist of a state-selection inhomogeneous electric field (A), a resonance region (c), and a state analyzer (B). Application of microwave or radio-frequency radiation in region C allows precise rotational spectra to be measured, yielding bond lengths, force constants, and dipole moments (via the Stark effect). Magnetic properties can be probed by introducing an inhomogeneous magnetic field into this region.

Our initial studies are planned for the alkali metals and the alkaline earth metals. Photoionization and electron attachment will be applied to these systems in an attempt to establish a series of measurements relating these properties to cluster size, spanning the region from the atom to the bulk. Structural information on trimers and larger clusters will be sought in pure metals as well as in mixed systems. These measurements will be extended to the transition elements Fe, Co, Ni, Cu, and Zn and to various alloy clusters.

ABSORPTION SPECTRA OF SOLIDS AND SOLID SURFACES

Principal Investigator: John S. Winn

The electronic properties of matter are best studied by absorption spectroscopy if one's primary interest is in the properties of the ground state. For solids and surfaces, these measurements are obviously difficult to make. The technique of optoacoustic spectroscopy is perhaps the simplest way in which such measurements can be made. The components of an optoacoustic spectrometer are shown in Fig. 1. A tuneable light source is modulated at some frequency by a chopper. The light energy is focused onto a small area of the solid, which is in thermal contact with a constant volume reservoir of a gas. When the light is absorbed by the solid, the energy is converted to heat, transferred to the gas, and measured as a pressure wave in the gas modulated at the light chopping frequency. The intensity of the pressure wave is proportional to the absorption coefficient of the solid at the wavelength of interest.

The resulting spectrum is unique in an important way. Not only will simple light absorption trigger a pressure rise, but also photodecomposition into a gaseous component of the solid or photodesorption of a gas from a surface will be detected as an increase in the total gas pressure above the ambient dark value. In this way, one can learn the spectral regions effective in selective excitation of solids or surfaces. The materials one can study are clearly numerous. The amounts needed are small—frequently a few milligrams will suffice.

We are beginning our studies with the metal carbonyls. These species are well characterized in the infrared, but their optical spectra have received little attention. Studies of photochemically activated catalysis or desorption from transition metal surfaces are similarly of interest.

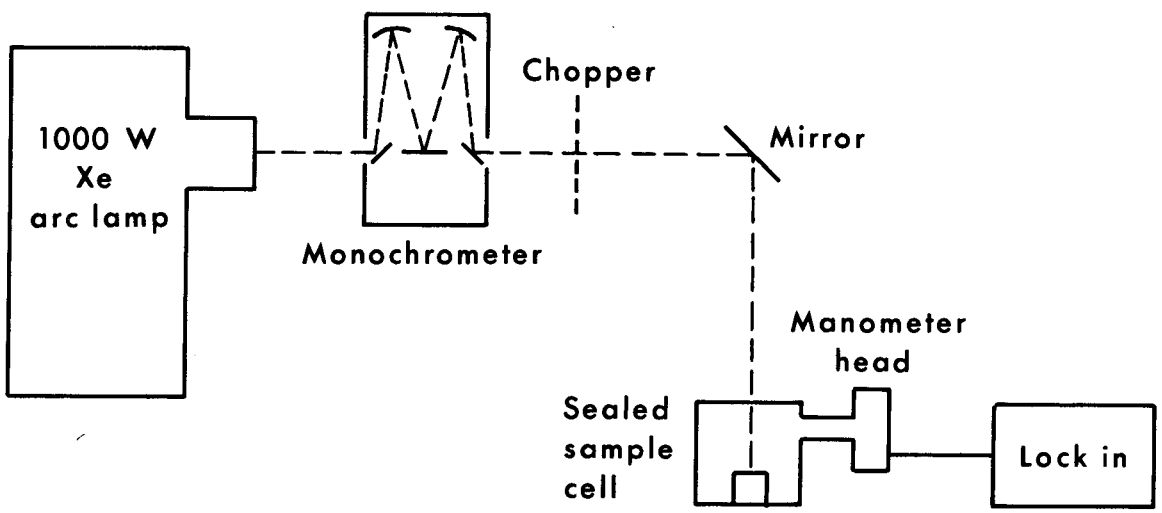


Fig. 1

STRUCTURAL MEASUREMENTS OF METAL-NONMETAL INTERACTIONS

Principal Investigator: John S. Winn

To understand the chemical nature of adsorption, heterogeneous catalysis, and metal-nonmetal interactions in general, the molecular structure of the system at hand is mandatory. For surfaces, this information is becoming available from LEED studies of the surface-adsorbate composition. For example, the Fischer-Tropsch reaction, H_2 + CO reacted to give hydrocarbons, requires an understanding of adsorbate-metal structures at the molecular level if we are to begin to design specific catalysts to guide the course of reaction toward a favored product.

We plan to study the metal-adsorbate bond beginning with one metal atom and one adsorbate molecule: FeCO, for example. The technique is the molecular-beam electric resonance method of measuring rotational spectra. These spectra will give high-resolution data on bond lengths, angles, force constants, and bond energies. Clues to the electronic structure of the molecule can be found from nuclear quadruple-coupling hyperfine measurements in many cases.

The sources of molecules for study are varied—indicative of the wide range of species open to investigation. A mixed system of metal vapor and adsorbate gas (Ar, H_2, CO, CO_2, N_2, H_2O, etc.) can be expanded from a supersonic nozzle and will produce varying fractions (depending on source conditions) of free atoms, metal clusters, and metal-nonmetal molecules. Alternatively, organometallic compounds and metal or polymetal carbonyls can be disrupted via discharge, photolysis, or thermal decomposition to yield small molecular fragments for study. Particularly attractive is the possibility for production of species such as $Fe_3 \cdot CO$, which approach realistic surface-adsorbate systems by including more than one metal atom.

ELECTRONIC STRUCTURE OF SURFACES USING PSEUDOPOTENTIALS

Principal Investigator: Marvin L. Cohen

The importance of solid-vacuum (surfaces) and solid-solid interfaces to problems such as energy conversion, control of pollutants through catalysis, electronic devices, etc. is well-known. The reactive nature of surfaces in the above applications depends on the behavior of the surface electrons. From the point of view of a solid-state physics theorist, this is a difficult problem because of the lack of symmetry one has to contend with in doing surface calculations. In bulk crystals (which theorists assume to be infinite and periodic), there are methods that rely on the crystal periodicity in all three dimensions. These methods are capable of giving accurate information about electrons in the bulk solid. The empirical pseudopotential method is an example of such a scheme. Accurate potentials describing the interaction of electrons with the ions in a solid can be obtained, and in turn the energy spectrum, charge density and a host of properties of solids can be calculated. The extension to surfaces of this type of approach is not simple because of the loss of periodicity and its consequences.

We have recently been successful in developing a scheme similar to the bulk pseudopotential calculational methods. Instead of giving up the periodicity necessary for the calculational procedures, we construct large cells—supercells—containing the configuration of interest, and repeat these infinitely. For a surface, the supercell retains the usual crystal symmetry in two dimensions in the plane perpendicular to the normal at the surface. To simulate the surface in the third direction, the cell contains a slab of the crystal. The result is an infinite array of slabs of crystalline material with identical properties even though we are only interested in one cell.

One other important problem has to be surmounted before successful surface calculations can be done. Electrons at a surface experience a different electron-ion potential than in the bulk crystal. This is primarily because the electron density readjusts at the surface and screens the ions differently than in the bulk; in addition the positions of the ions may be different at the surface. This rearrangement of electrons must be evaluated accurately. In the scheme used here, the readjustment is accomplished through the <u>self-consistency</u> requirement. The calculation is first done with ion potentials in bulk positions. The resulting electron density is then used to create screening potentials, and the ions are moved to their assumed surface positions. The calculation is done again with the adjusted electronic density. The new result is then fed back in until the electronic spectrum ceases to change and the electron density remains stable.

The method has been extremely fruitful. After initial checks involving calculations of bulk properties and molecular spectra for comparison, a host of calculations was done. Silicon was used as a semiconductor prototype, and the electronic structure of the surface was explored in detail. Charge density plots illustrated how electrons could be localized at the surface and "showed" the real space location of the electrons, in addition to

giving the usual k-space configuration, which is usually familiar only to solid-state theorists. Calculated electron energy spectra could be compared directly with experimental measurements such as photoemission and optical spectra. The method was then applied to other materials like group IV, III-V and II-V semiconductors. Models containing adsorbates like hydrogen and chlorine on silicon, stepped surfaces, and simple metal surfaces were explored successfully.

A very detailed calculation of the metal-semiconductor interface or Schottky barrier was done. This calculation showed that all previous theories of Schottky barrier behavior were insufficient to explain the properties of this important device. The calculation led to a new detailed explanation of the electronic structure near a metal-semiconductor interface.

Because of the importance of transition metals in surface physics and chemistry, considerable effort was expended to obtain the energy spectrum for a niobium surface self-consistently. The calculation gave pictures of surface states and energy spectra, but required considerably more computer time than the semiconductor or simple metal cases. Adsorbate calculations that used this approach seemed untenable. However, new developments described below seem likely to change this picture considerably.

Extensions of the above calculations are currently in progress. Schottky barriers, heterojunctions, and solid-vacuum interfaces are being explored by using the methods described above. Because of the extensive computer time required for transition metal-surface calculations using pseudopotentials, we have been limited up to now in our studies of adsorbates to the use of tight-binding methods. These methods are useful, but because they are not self-consistent they lack reliability. Fortunately, quite recently, we have been successful in using a "mixed-basis set," which uses plane waves for s and p electrons and localized waves for d electrons. This method, together with our self-consistent pseudopotential approach, appears to have the flexibility and power to bring our transition metal-surface calculations up to the level of our semiconductor surface calculations without requiring excessive computation time.

RESEARCH ON GRAIN BOUNDARIES AND PHASE BOUNDARIES IN MATERIALS

Principal Investigators: J. William Morris and Gareth Thomas

The surfaces that are important in engineering materials include not only the external surface but also internal surfaces which may have a critical influence on chemical and mechanical properties. Most materials of engineering interest are polygranular (Fig. 1). They consist of microscopic crystallites of material delimited by grain boundaries. Moreover, engineering materials are often polyphase, containing two or more chemically distinct phases separated by interfaces.

The internal surfaces have complex properties and important consequences for engineering behavior of the material. These surfaces are only beginning to be understood as modern research techniques are applied to their study. These internal boundaries separate crystalline grains, and hence have a detailed structure of their own, which changes with the crystallography of the grains they bound and may also change with time as the boundaries act as sources and sinks for dislocations and point defects. The boundaries also have a complex chemistry of their own as they attract or repel species present in the bulk according to interactions, which vary with their detailed structure.

The influence of internal surfaces on material properties is always important and often critical. The boundaries often act as catalytic sites for phase transformations, precipitation reactions, and cavitation or void nucleation, hence influencing materials processing and property degradation during service. The boundaries strongly affect plastic deformation and fracture by acting as sources and sinks for crystal dislocations and by governing the transmission of dislocations (hence the accommodation of plastic flow) to adjacent grains. At high temperature the boundaries may directly contribute to plastic flow through grain boundary sliding. The boundaries may contribute to fracture in catastrophic ways. The accumulation of deleterious species or precipitate films within the boundary may lead to brittle intergranular failure under very low loads in a material which is otherwise strong and tough. Deleterious chemical species in the boundary may also render an alloy susceptible to stress corrosion cracking, again causing unanticipated failure under low loads in service.

Given the importance of grain- and phase-boundary properties to engineering materials, and the availability of probative new research tools for studying these boundaries, there is a growing research activity within MMRD in grain boundary structure and properties. Current research projects in our research groups cover a spectrum of topics from basic theoretical and experimental studies of the structure of boundaries to applied research on techniques for overcoming grain boundary embrittlement in promising engineering alloys. Specific projects include the following:

1) <u>Grain Boundary Structure</u>

The principal theoretical tool used in the study of grain boundary distribution and structure is computer simulation, either on the atomic scale, where one attempts to determine the precise configuration of atoms at a grain boundary of particular type, or on the continuum scale, where one examines the distribution of grain boundaries through

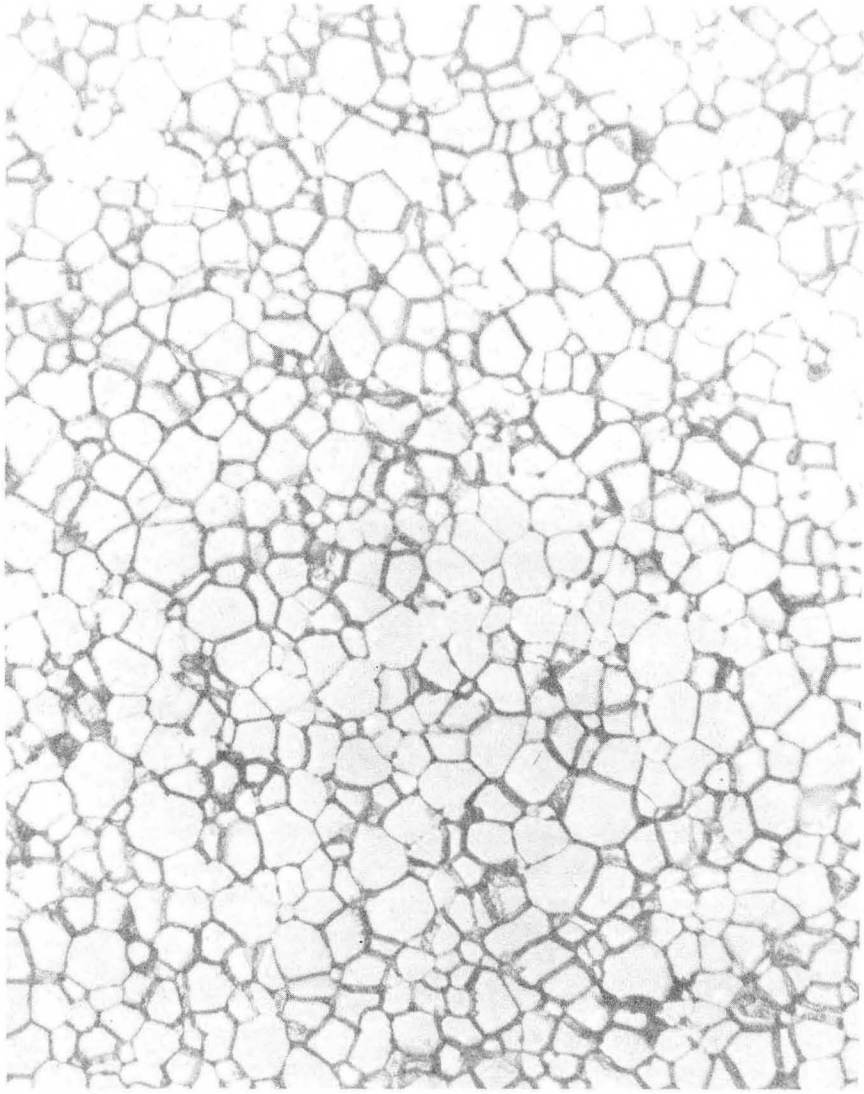


Fig. 1. The microstructure of Armco iron showing crystalline grains separated by grain boundaries (light micrograph, 500X).

the body of a material. Both approaches are being taken in current research at MMRD. In atomic simulation studies (Hong and Morris) semi-empirical interatomic potentials are used to study the relaxation of the crystal structure of adjacent grains near a boundary of given type. An example of a simulated grain boundary structure is shown in Fig. 2. The results of these simulation experiments give insight into grain boundary structures and suggest the structural source of chemical and mechanical properties. In microstructure simulation studies (Mahin, Hanson, and Morris) plausible nucleation and growth laws are used to simulate microstructures of the types which may result from solid-state reactions. These simulations generate realistic distributions of grain boundary locations and types through the material. These distributions are needed in theoretical studies of diffusional processes and mechanical behavior dominated by grain boundaries.

The principal experimental tool used in studies of grain boundary structure is high-resolution transmission electron microscopy. By using lattice imaging techniques, a spatial resolution of ~1.5Å can be achieved, and allows the direct imaging of the planes of atoms in adjacent crystals as they impinge to form the grain boundary. As a specific example, this technique is being used (Clarke and Thomas) to study the structure of grain boundaries in hot-pressed silicon nitride, a prime candidate material for use in high-temperature turbines. Silicon nitride exhibits a dramatic decrease in strength above about 1000°C, which has been attributed, on circumstantial evidence, to the presence of a glassy phase in the grain bound-

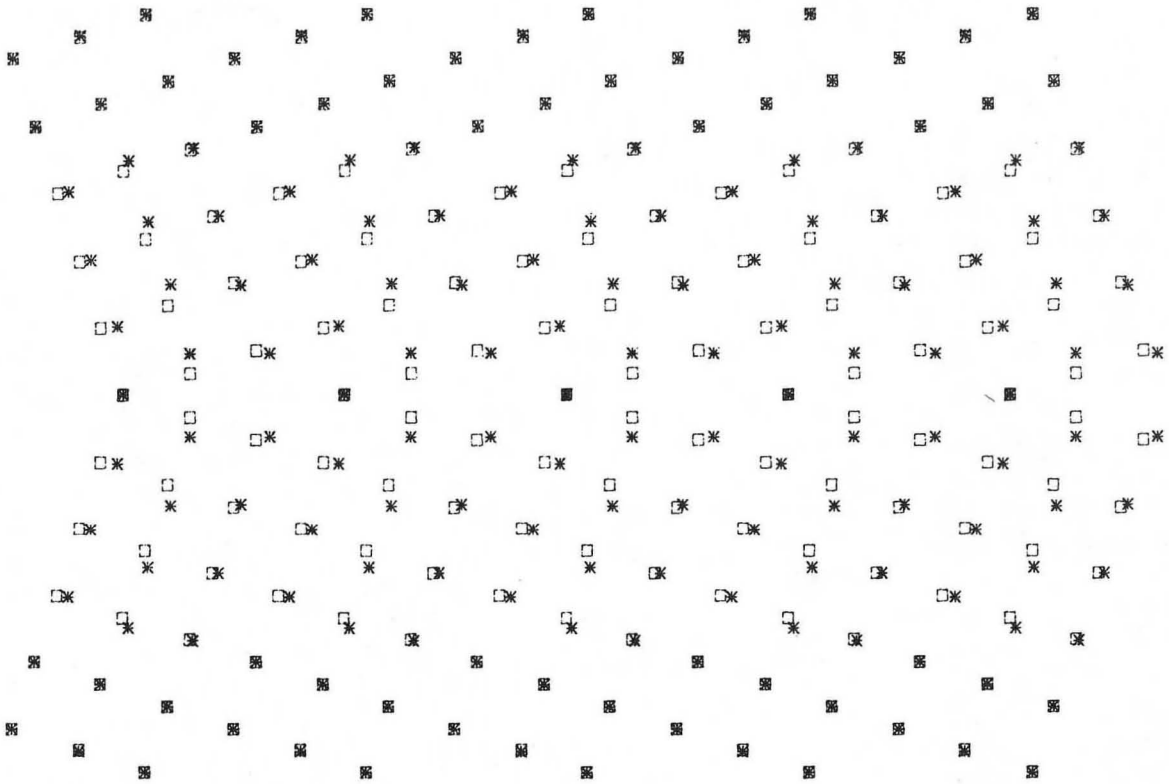


Fig. 2. The configuration of atoms near a grain boundary in aluminum, computed on the assumption that the atoms interact according to the Morse potential. The symbol (□) shows the crystallographic atoms sites before relaxation. The symbol (*) shows atom positions after the lattice has relaxed to accommodate the surface defect.

aries. Direct observation of the grain boundary structure through lattice imaging (Fig. 3) shows, however, that while a glassy phase exists, it does not penetrate the grain boundary; it rather appears to be strictly confined to the junctions at which three grain boundaries meet one another. This recent experimental result necessitates a basic rethinking of the "sand and molasses" model of high temperature deformation, a process which will certainly lead to a better understanding of high-temperature mechanical behavior.

In related work (Gronsky and Thomas), lattice imaging techniques are being used to characterize the interfaces of growing precipitate particles in alloy systems. All relevant theories suggest that the velocity of the moving interface, and hence the rate of transformation, is strongly dependent on the interface structure. The example illustrated in Fig. 4 shows growth along two low-energy precipitate interfaces in an Al-Zn alloy, and demonstrates that a ledge mechanism (see arrowed ledges) dominates growth. One of

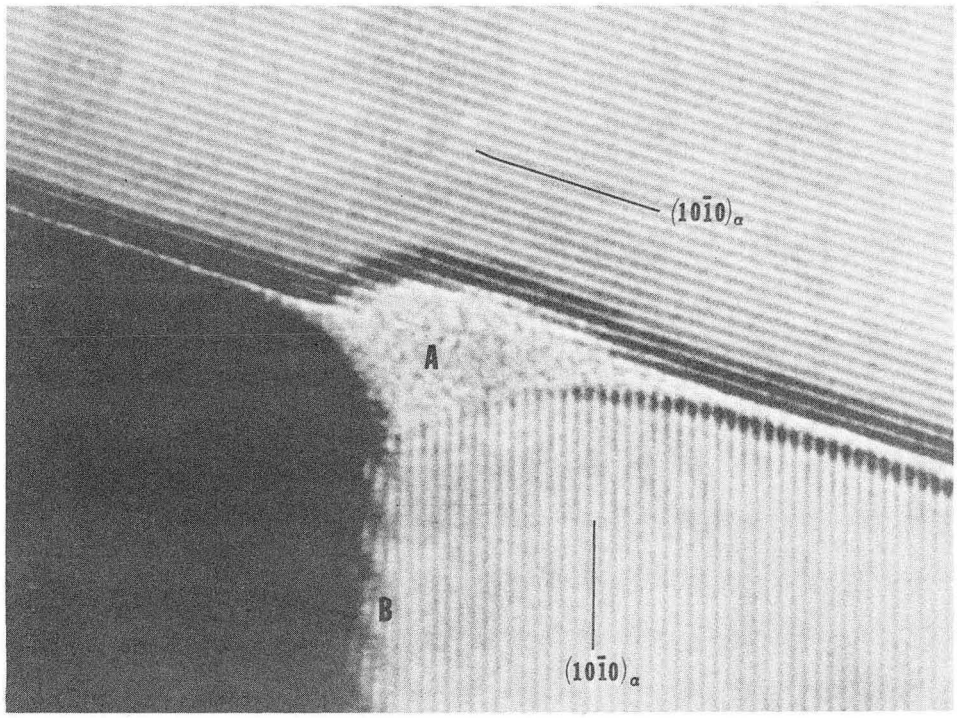


Fig. 3. Triple-point region in a hot-pressed, 5% MgO, silicon nitride material. The lattice fringe image reveals the $(10\bar{1}0)$ planes in adjacent grains and indicates the presence of a second phase at the triple point A.

the ledge facets imaged in the figure parallels the low-index lattice planes within the precipitate (a), while the others parallel low-index planes in the contiguous grain (b). Observations of this sort provide clear guidelines for theoretical studies of precipitation kinetics.

The toughness of high strength, tough martensitic steels has been examined in a series of experimental Fe/Cr/C base steels. An important result which has been obtained by high resolution TEM and electron diffraction is that thin films (~100 Å) of retained austenite occur between the narrow martensite laths (~0.5 μ wide). These films appear to contribute to high toughness. However, on tempering at ~300 - 400°C these films break down to a carbide and cause a loss of toughness; i.e., a special type of temper embrittlement occurs. Critical questions associated with the stability of the austinite are associated with solute distribution. Clearly, chemical analysis of these retained γ films and their decomposed products on tempering will lead to a better understanding of austenite stability and be an important contribution in the alloy design program.

A successful new series of high strength Fe/2Si/0.1%C steels heat treated to form duplex ferrite martensite structure have been developed, which appear to be

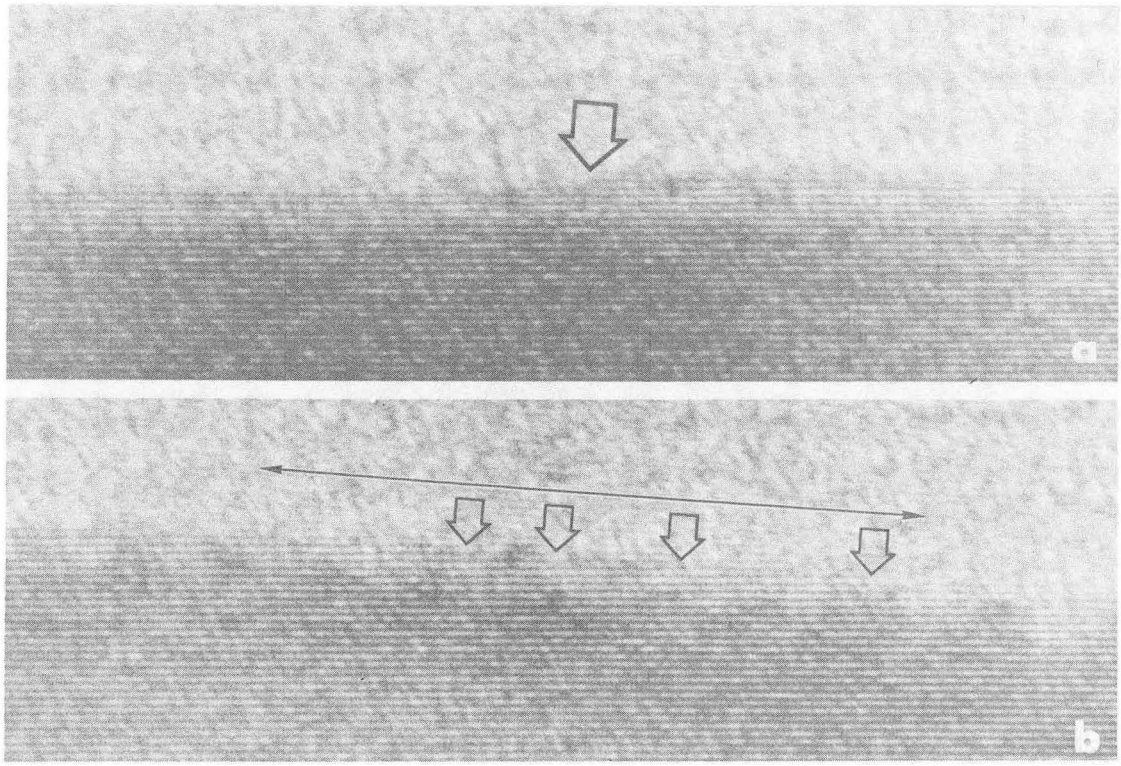


Fig. 4. Atomic steps (ledges) at a grain boundary viewed edge-on in Al-30Zn aged 1 week at 20°C.

competitive for energy saving applications (e.g., automobiles) and as substitutes for HSLA steels. The strength of these duplex alloys is related to the strength and volume fraction of the two phases which in turn are related to their composition. Due to the fineness of the structure, techniques such as Auger analysis are urgently needed to analyze these phases and to find out the solute distribution. The role of Si in expanding the $\alpha + \gamma$ two phase fields can then be analyzed so as to guide us in future design programs.

The studies mentioned here clarify the physical state of interfaces. Modern analytical tools also permit a detailed chemical characterization of the interfacial region. We hope to procure equipment in the future that will permit chemical characterization to be carried out simultaneously with lattice imaging studies.

2) Grain Boundary Influence on Plastic Deformation

The influence of grain boundaries on the plastic deformation of engineering materials is being studied both analytically through computer simulation, and experimentally through research on superplastic creep, where the grain boundary influence is most striking. In computer simulation experiments (Hanson and Morris), the grain boundary is modeled as a simultaneous physical and crystallographic barrier to the motion of dislocations, which may "pile up" at the boundary, be absorbed into the boundary to result in grain boundary motion, or cross the boundary to transfer deformation from one grain to another. The dominant process depends on the nature of the boundary, the crystallographic misorientation between grains, and the density of dislocation or dislocation sources. Simulation codes are now being constructed to examine these processes in detail.

The deformation directly due to the sliding motion of grain boundaries is most pronounced in superplastic deformation. This high-temperature deformation process is now under study (Grivas and Morris) through creep experiments, which will shortly be expanded to electron microscopy studies. The role of grain boundaries in superplastic deformation remains poorly understood, though it is known to be important. Current theories emphasize the role of the grain boundary as a sink for crystal dislocations. However, evidence recently obtained at Berkeley may be more consistently explained on the hypothesis that the role of the grain boundary as a source of dislocations is critical. If this hypothesis is verified it suggests new interpretations of a number of interesting aspects of high-temperature deformation.

3) Grain Boundary Influence on Fracture

Grain boundaries always effect the fracture stress of engineering materials. Their most striking and deleterious effect occurs when the boundary becomes a source of brittleness, leading to catastrophic intergranular failure under low load. Current research at MMRD addresses both the sources of grain boundary embrittlement and the development of practical metallurgical techniques to overcome it. This research particularly addresses problems of grain boundary embrittlement in the new alloys for cryogenic systems under development at MMRD.

Grain boundary embrittlement is particularly severe in ferritic Fe-Mn alloys, and is the principal barrier to the use of cryogenic

systems. The problem is illustrated in the upper fractograph of Fig. 5, which shows the intergranular fracture mode in Fe-12Mn-0.2Ti broken in liquid nitrogen. Research at MMRD (Hwang and Morris) has shown that the intergranular fracture may be suppressed by treating the alloy to refine the grain size and to control the distribution of phases on the microstructural level, as illustrated in the lower fractographs of Fig. 5.

The metallurgical processes used to control intergranular fracture in Fe-Mn alloys are complex, and would add significantly to the cost of using the alloy in commercial practice. Research toward simpler techniques is hence important. The success of this research depends on a detailed understanding of the source of grain boundary embrittlement. Fundamental studies emphasizing Auger spectroscopy and ESCA analysis are under way. The results obtained to date are inconclusive, but suggest that the embrittlement problem may be inherent in Fe-Mn alloys, due possibly to an accumulation of Mn in the grain boundary. If this hypothesis is established through further work, it should be possible to eliminate intergranular fracture through suitable modifications of the alloy composition.

The commercially available ferritic cryogenic steels (Fe-9Ni, Fe-5Ni) are toughened for cryogenic use through thermal treatments, which add a small amount of the high-temperature γ-phase in the grain boundary of the ferritic alloy. The precise role of this γ-addition is not known, but must be understood if the engineering shortcomings of these alloys (high cost and poor proerties at temperatures below 77°K) are to be overcome. In current Mössbauer spectroscopy and transmission electron microscopy are used to specify the amount and distribution of austenite and to determine the mechanical stability of the austenite in the highly deformed material near propagating cracks. The available data suggest that a major beneficial effect of the austenite is to "getter," or remove deleterious chemical species from the grain boundaries. Precise chemical analysis of surfaces before and after austenization will be required to clarify this behavior.

Future projects which we hope to undertake at MMRD include research on grain-boundary catalyzed phase transformations, on temper embrittlement in steel, and on stress corrosion cracking due to grain boundary sensitization. Each of these studies ultimately addresses engineering problems that are important to the ERDA mission. Our potential success in each of these areas depends critically on the availability of advanced surface-analysis equipment and on the presence at MMRD of an interdisciplinary group of investigators who are knowledgeable in the theory of interfaces and in the experimental use of the most advanced analytical tools.

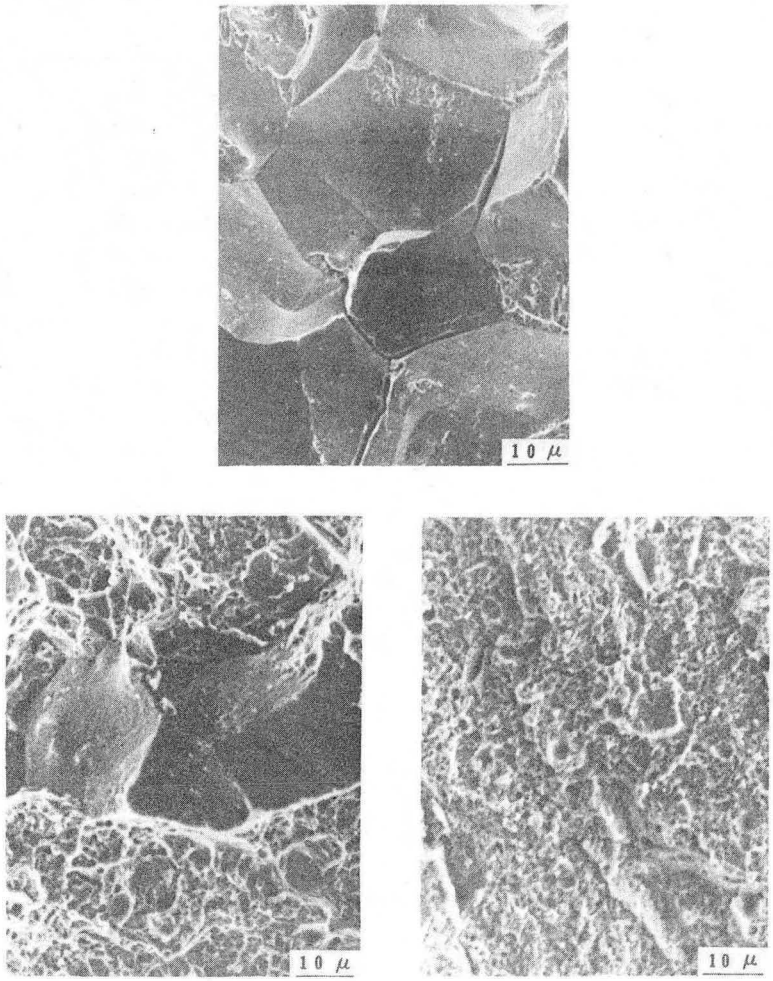


Fig. 5. Scanning electron micrographs of fracture surfaces in Fe-12Mn-0.2Ti broken in liquid nitrogen. The upper figure shows intergranular facture in the quenched alloy. The lower micrographs show that intergranular fracture may be partially suppressed by suitable tempering (lower left) and fully suppressed by a cold work + annealing treatment (lower right).

SURFACE LAYERS IN CONTACT WITH CONDENSED MEDIA: OBSERVATION BY ELLIPSOMETRY

Principal Investigator: Rolf H. Muller

Analysis of the elliptic state of polarization that results from the reflection of polarized light (ellipsometry) provides an extremely sensitive measure for the observation of surface layers and microtopographies. The substrates can be contained in any medium that is optically transparent, such as liquid or gas. Surface coverages from less than 1% of monomolecular coverage to micron thickness can be determined. The unique automatic ellipsometer built in this laboratory is also capable of following film growth at rates up to a few micrometers per second.

From the two measured ellipsometer parameters, we can derive the thickness and optical properties of surface layers. We have been able to infer information on composition and porosity that has subsequently been confirmed by independent means. In ultrahigh vacuum, we have determined adsorption isotherms, heats of adsorption, and molecular cross sections.

Recent efforts have been directed towards understanding the optical effect of mass-transport boundary layers. Since these effects are unavoidable present in heterogeneous reactions proceeding at finite rates, they have established ellipsometry as a new technique for the measurement of interfacial concentration of reacting species.

Ongoing studies on the electrochemical generation and transformation of surface layers give conclusive evidence of a dissolution-precipitation mechanism of anodic oxide formation for several metals. Zinc is shown as an example in Fig. 1. The two measured ellipsometer parameters ψ and Δ, starting from the values for bare Zn, first indicate roughening of the metal surface; dissolved reaction products can then be observed to accumulate near the surface. After saturation concentration is reached, the growth of a solid, passivating film sets in, with the observed film growth reasonably following computed points for film thicknesses up to 600 Å. The <u>in situ</u> identification of surface compounds will be further advanced by the planned addition of spectroscopic capabilities to the ellipsometer.

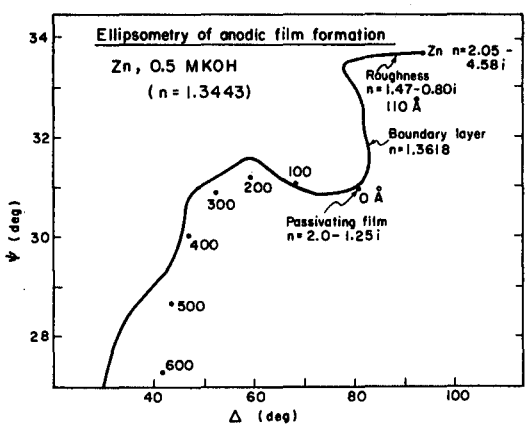


Fig. 1

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