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Report of an Advanced Light Source Workshop on CHALLENGES FOR INTERFACE THEORY

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CHALLENGES FOR INTERFACE THEORY

Lawrence Berkeley Laboratory
Berkeley, California
August 20 – 24, 1990

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1. Introduction

This report summarizes the findings of a Workshop whose aim it was to identify challenges for theory in the field of surfaces and interfaces, and to point at directions for future theoretical research. The main recommendations are highlighted in the executive summary (section 5). Particular emphasis was put on new opportunities that will be provided by the advent of a new generation of synchrotron radiation facilities in the mid-1990s. This includes the Advanced Light Source (ALS) which is now under construction at Lawrence Berkeley Laboratory and is scheduled to be put in service in 1993. The Workshop Program is included in the Appendix.

Surface and interface science enjoys a unique and very close dependence on interaction between experiment and theory. The many important basic phenomena in this field in most cases can only be understood and modeled with sophisticated theoretical methods, analogous in complexity to those developed in the solid state and in molecular quantum chemistry. As an example, a feature of much experimental work on surfaces and interfaces to be carried out at the ALS and similar facilities elsewhere is the frequent use of low-energy electrons as emitted probes. Theory often is needed to clarify what information these electrons convey about surface properties. Also with photon-only experiments, theory is frequently required to interpret the data or understand the underlying significance and mechanisms.

As a result, theory will be in great demand and it is wise to identify not only the new opportunities for theorists, but also the needs of the experimental community. The interplay between experiment and theory has always been strong and will grow. This is borne out by the numerous contributions from experimentalists to this workshop and this report.

Our report discusses many topics that will provide fruitful areas of research for many years to come at the confluence of physics, chemistry and materials science. Both the problem areas and theoretical approaches to solving them are considered. Purely experimental issues will not be emphasized. An excellent review exists which identifies the scientific opportunities as well as experimental issues expected with the next generation of synchrotron radiation facilities, and at the ALS in particular: W. Eberhardt and C.S. Fadley, "Summary of Workshop on New Opportunities in Surface Science at the Advanced Light Source", LBL report PUB-5215 (Sept. 1988).

The ALS will accelerate electrons to 1.5 GeV and use undulators and wigglers to generate photons predominantly in the soft-x-ray range (energy of 10-1000 eV, wavelength of 10-1000 Å). The undulators will yield high-brightness photon beams with tunable peak energies and narrow time structure. A number of exciting new experiments will thus be possible, as considered in more detail in the above-mentioned report.

Of special interest to the Berkeley scene is the programmatic overlap between the planned surface and interface studies at the ALS and research at other LBL facilities. In existence already is the National Center for Electron Microscopy (NCEM), which has provided atomic-resolution imaging of many types of interfaces. Very fruitful collaborations can also be foreseen with the planned Combustion Dynamics Facility, which is to attach an infrared free-electron laser to the ALS and also provide a theoretical effort in order to investigate combustion mechanisms, including those occurring at surfaces.

In the next section, this report addresses atomic structure, i.e. the geometric positions of atoms at surfaces and interfaces, including techniques for studying structure. Then, in section

3, the electronic structure and theoretical methods for determining it are discussed. Section 4 takes up the issues related to surface reactions and dynamics. Finally, section 5 summarizes the most important issues that emerge for the near- to mid-term future.

2. Atomic Structure

The atomic bonding arrangement at surfaces is fundamental to many surface processes. Close to 300 surface structures have so far been determined in detail, at the picometer level of atomic coordinates, bond angles and bond lengths. Many more structures are known approximately or incompletely. **Significant developments in recent years have provided structural information of greater accuracy for more complex surfaces that are also technologically more relevant than before. But even more structures need to be solved, especially for a greater variety of surfaces** (e.g. for compounds and for systems with some disorder). This will yield a more fundamental and broad understanding of all processes at surfaces.

Great progress can also be recorded in the theoretical understanding and modeling of surface structure. **Total-energy calculations are increasingly able to predict the observed structural details. Substantial progress has been achieved in understanding more complex systems, including surface reconstruction and the effects of adsorption. A great deal remains to be done to extend such understanding to more relevant surfaces and to processes like diffusion, phase transitions, surface segregation, surface reactions, etc.**

A multitude of modern experimental techniques has contributed to these results. Many of these techniques rely strongly on theory for the data interpretation. Most prominent among the currently used techniques are:

- LEED: low-energy electron diffraction
- ICISS: impact collision ion scattering spectroscopy
- MEIS and HEIS: medium- and high-energy ion scattering, also called Rutherford back scattering (RBS)
- ARPES: angle-resolved photoelectron spectroscopy, including both core and valence level studies
- PD, AED, etc.: diffraction and forward focusing (FF) of photoelectrons, Auger electrons (AED) and inelastic electrons, including the novel electron holography (EH)
- SEXAFS: surface extended x-ray absorption fine structure
- NEXAFS: near-edge x-ray absorption fine structure
- XRD: x-ray diffraction
- REM and TEM: reflection and transmission electron microscopy, and other forms of (high-energy) electron microscopy

- STM: scanning tunneling microscopy and related microscopies
- HREELS: high-resolution electron energy loss spectroscopy
- PEM: photoelectron microscopy; LEEM: low-energy electron microscopy; and other related microscopies
- PSD and ESD: photon- and electron-stimulated desorption

Several of these techniques depend on or benefit greatly from synchrotron radiation, such as ARPES, SEXAFS, XRD, PD, AED, forward focusing, PEM and PSD. These will be thrust into a next generation of utility and precision when the new synchrotron radiation facilities are put in service.

It remains true today that many problems in surface/interface science cannot be solved by one technique alone. Especially when the complexity increases, as will happen more and more, several different experimental and theoretical techniques must be used side by side to analyze and understand structure and properties.

A major challenge is the solution of complex structures with many unknown structural parameters. Related to this is the need to attack a wide variety of useful materials that have so far barely been explored, from simple compounds to biologically-relevant molecules.

We shall in the next subsections first summarize the main structural features that have been identified at surfaces in recent years. Then progress in technique development will be reviewed, focusing on both past and anticipated theoretical developments.

2.1 Clean Surfaces: Relaxations and Reconstructions

It has long been known that atoms in many clean surfaces relax away from their ideal bulk lattice positions. In many cases reconstruction results, especially on semiconductor surfaces. Theoretical understanding of these effects is generally firm, but often minute energy differences between competing structures make predictions uncertain. Theoretical accuracy is thus at a premium, resulting in expensive computations which should be made more efficient.

More complex are issues related to compound materials. Of central concern is the composition of a compound in the near-surface region (within about 10 Å from the surface), which can vary drastically from that in the underlying bulk. Prediction is still hazardous in this respect and much progress is desirable here.

We now address our knowledge and expectations of surface structure and related properties for different categories of materials.

2.1.1 Elemental Metals

The surface structures of elemental metals are the best known and understood among all materials, thanks to their relative ease of preparation and control, and also due to their frequent relative structural simplicity. **In these materials, multilayer relaxations and reconstructions have been extensively analyzed with the greatest accuracy.**

This has allowed further progress in exploring kinetic and dynamical effects, such as atomic diffusion and phase transitions, including roughening and melting. Simple stepped metallic

surfaces have already been analyzed in some detail: "kinked" stepped surfaces remain to be addressed, as well as wide-terrace structures. This is becoming possible thanks to new theoretical methods in the multiple scattering of electrons.

Notable theoretical achievements have been recorded in determining the reconstruction of metal surfaces, especially for Ir, Pt and Au(100) and (110), as well as Au(111), Mo(100) and W(100). Understanding of the origin of these reconstructions has progressed particularly for the (110) "missing row" structures, and the Mo and W(100) structures.

Techniques that have been particularly successful in the study of clean elemental metals include LEED, ICISS, MEIS and HEIS, and lately but with less accuracy, forward focusing of electrons.

2.1.2 Alloys

It is a challenge for both theory and experiment to determine the energetics of alloy formation. Knowing the atomic structure of a bulk alloy gives significant information about the bulk phase diagram. **At interfaces and surfaces, the formation of alloys is much less well understood than in the bulk and direct thermodynamic measurements are extremely difficult, if not impossible.**

Progress has been achieved with the structure determination of several ordered binary alloys, which exhibit easily detectable relaxations. With surfaces of disordered binary alloys, it has been possible to detect very strong layer-by-layer fluctuations of the composition within the first few surface layers.

Information about the local structure of alloys in small portions of a sample should be accessible from experiments using high brightness synchrotron light sources, complementing LEED. Forward focusing in particular appears very promising in this regard. Total-energy electronic structure calculations can also provide information about the energetics of low temperature alloy formation (neglecting kinetic effects). In the future, these types of calculations should be able to address questions of kinetics and temperature effects.

2.1.3 Elemental Semiconductors

Although surface reconstruction was first observed on silicon, the solution of the surface structures of elemental semiconductors came much later than for metals. **The complexity of the semiconductor reconstructions required a prolonged multi-technique and multi-laboratory approach.** Particular success has been achieved with TEM, STM, MEIS and HEIS, LEED and XRD. **Theory has contributed greatly to understanding the observed reconstruction mechanisms.**

A major achievement came with the solution of the structure of Si(111)-(7x7). The complexity of this reconstruction required many years of efforts by many different research groups using the entire panoply of surface science techniques. The Ge(111)-c(2x8) reconstruction is now also solved. Theory has had an important role in understanding the causes of these *a priori* unexpected reconstructions, even without being able to perform accurate calculations due to the large and complex unit cells.

Nevertheless, many details of the surface reconstructions of elemental semiconductors are still under debate. For instance, it is not yet settled whether the dimers in the Si(100)-(2x1)

reconstruction are symmetrical or buckled. There are similar questions involving the Si(111)-(2x1) reconstruction: does dimerization occur in the π-bonded chains? And these questions have been investigated even less for the Ge and C (diamond) surfaces.

2.1.4 Compound Semiconductors

A considerable number of surface structures has been obtained for non-polar faces of compound semiconductors. These include foremost the (110) surfaces of III-V zincblende materials (GaAs, AlAs, GaP, etc.), but also surfaces of wurtzite materials (ZnO, CdS, etc.). These do not reconstruct into a larger unit cell, but do exhibit large relaxations due to strong rehybridization in the topmost layer. **The polar faces of such compounds**, however, **tend to reconstruct**, for instance with vacancies due to missing atoms and with substantial relaxations due to rehybridization.

LEED has been the foremost technique applied to these surface structures, with valuable contributions from XRD for the reconstructed cases. The theoretical understanding of the origin of these surface structures is quite good, although not quantitative.

On the other hand, there is still a lack of high-accuracy structural data, without which a systematic analysis of differences across the periodic table cannot be achieved.

2.1.5 Oxides and Other Compounds

Despite their considerable importance for such processes as corrosion and catalysis, **most oxide and other compound surfaces have not been studied in any structural detail.** Only a few simple structures are known, such as NiO(100) and MoS_2(0001). Experimental preparation and measurement for many such materials are often considerable challenges. As with metallic alloys, **the question of surface composition (stoichiometry) is most important and poorly understood.** Very little theory has been devoted to the modeling of such compound surfaces.

LEED has been the main structural technique applied to such surfaces. Forward focusing and MEIS/HEIS should be ideal for their further study.

2.1.6 Relaxations

In recent years it has become abundantly clear how prevalent atomic relaxations are at surfaces. Most clean surfaces show some contractions. Only a few surfaces have escaped the observation of relaxations.

Multilayer relaxations perpendicular to the surface and extending several layers down below the surface have been documented in many studies of less close-packed surfaces, i.e. of the rougher (more open) surfaces. At least for clean elemental metal surfaces, one usually finds a contraction of the topmost interlayer spacing, followed by an expansion of the next deeper spacing, then mostly a contraction in the next layer, etc., with relaxation amplitudes decaying away from the surface. Alloy surfaces have also been found to relax, as have some binary oxides. Accuracies in atomic positions now approach 1 picometer (0.01 Å) for clean metal surfaces.

Clean surfaces with lower symmetry parallel to the surface, such as stepped surfaces, also

exhibit lateral relaxations. So far, only stepped surfaces with narrow terraces between adjacent steps have been analyzed. New methods, introduced recently, will allow wider-terraced surfaces to be investigated as well.

Theory is able to predict such relaxations rather accurately. For instance, the embedded atom method, despite its approximations, has provided much information on relaxations to a depth of many layers.

2.1.7 Reconstructions

Reconstructions involve relaxations that enlarge the surface unit cell or large displacements that lead to non-bulk-like bonding arrangements, or both. They are the rule at semiconductor surfaces. Remarkable progress has been achieved in solving clean semiconductor reconstructions, including Si(111)-(7x7) and Ge(111)-c(2x8). Some metal surfaces also exhibit reconstructions, now well established. **A wide variety of types of reconstruction is observed, depending on the material and the exposed crystallographic surface.** They include, on metal surfaces, bond length contractions parallel to the surface and microfacetting, and, on semiconductor surfaces, bond angle changes due to rehybridization as well as changes in stoichiometry. Reconstructions are almost always accompanied by complex multilayer relaxations.

Extended multi-technique investigations have been required to resolve the details of these complex structures, a process that is far from complete even for many of the simpler cases.

The theoretical understanding of surface reconstructions has made great strides in recent years. Many methodologies have been proposed to explain the very diverse types of reconstruction that are observed.

2.2 Atomic and Molecular Adsorption

Adsorption on clean substrates models a vast array of technologically important processes, from catalysis to tribology, and including corrosion and electrochemistry, growth and epitaxy. **Significant progress has been achieved in the structural determination and understanding of atomic and molecular adsorption, although with less accuracy than in the case of clean surfaces. But much remains to be done, particularly in the areas of adsorbate-induced restructuring of the substrate and of molecular adsorption.**

A significant development has been the structural study of disordered adsorption, thanks to new instrumentation and theoretical methods. It is now possible to determine the detailed adsorption geometry of atoms and molecules bonded without long-range order but with well-defined sites on a substrate.

In the near future, the study of adsorption structures at stepped surfaces will be possible. This will provide much-needed access to the understanding of the role of surface defects in surface reactions.

2.2.1 Atomic Adsorption

The most impressive recent development in the study of atomic adsorption is the prevalence of adsorbate-induced relaxations found on metal surfaces. Thanks

to modern methods for simultaneously determining many structural parameters, it has become clear that one should expect detectable induced relaxations in the substrate in many situations. Such relaxations range from minor displacements from the clean-surface positions to major restructuring, and includes the possibility of subsurface penetration, i.e. absorption.

Another achievement is the determination of a number of adsorbate structures on semiconductor surfaces, primarily involving metallic adsorption to model the semiconductor-metal interface. These were until recently inaccessible because of their complexity, since the adsorption usually induces both reconstruction and large substrate relaxations.

Atomic adsorption at defect sites, steps, kinks, point defects and near coadsorbed species need to be studied. And atomic adsorption at non-metal and non-semiconductor surfaces, largely ignored so far, deserves much attention in the near future.

Many structural techniques have been successful for studying atomic adsorption. Major techniques employed include LEED, ICISS, MEIS/HEIS, ARPES, PD, AED, SEXAFS, STM and HREELS. Electron holography has already been successfully applied to atomic adsorption, although the spatial resolution needs to be improved.

Theory has provided a certain amount of understanding of atomic adsorption, ranging from adsorption sites and bond lengths to vibration frequencies and diffusion barriers. **A number of topics, such as adsorbate-induced relaxations, reconstructions and charge transfers, still need further study.** Also, theoretical work should be extended to other substrate materials.

2.2.2 Molecular Adsorption

Notable progress has been achieved in determining the adsorption structure on metals of molecules up to and including benzene in size. Large molecular distortions due to adsorption are found, which can be related to catalytic reaction processes. The adsorption of carbon monoxide on a variety of metal surfaces has been studied in much detail and still serves as a versatile research topic for many physical and chemical phenomena. To obtain insight into chemical surface reactions, it is imperative to broaden the scope of this work to a wider variety of related molecules, for example a family of substituted hydrocarbons. In addition, families of related substrates must be explored: different crystallographic surfaces and stepped surfaces, as well as different metals.

The phenomenon of coadsorbate-induced ordering has been observed to operate very effectively in mixed molecular layers: one type of molecule which does not order well by itself can order very rigidly when mixed in suitable proportions with another type of molecule. The most effective combination appears to mix electron-donating molecules with electron-accepting molecules.

Several techniques have proven most valuable in this area: LEED, NEXAFS and HREELS, while forward focusing of electrons promises to contribute substantially.

Molecular adsorption on non-metal surfaces and at steps are important directions for future investigations, for which the methodologies are currently already available. Of considerable interest for applications like lubrication would be the molecular layer sandwiched between two solid surfaces. Molecules at the solid-

liquid interface would be of great interest for electrochemical applications, among others.

2.3 Growth and Epitaxy

2.3.1 Growth

One of the technologically most important questions in materials science is how to make new materials and contacts between materials with atomic-scale control of their composition. With techniques such as molecular beam epitaxy (MBE), it is possible to adsorb controlled amounts of materials onto a substrate at the monolayer level. What can not always be controlled, however, is the growth mode, which is determined by a complicated interplay between equilibrium thermodynamics and kinetics. **The challenge for experiment and theory is two-fold:**

- **determining the actual growth modes;**
- **understanding and possibly altering those factors which control the growth.**

The first challenge will require knowledge of the atomic structure. The second challenge, specifically for theory, will be to disentangle the various contributions, including bulk effects, surface effects, distortion, lattice mismatch and kinetics. While the thermodynamic framework goes back to Gibbs, a complete quantitative and detailed qualitative understanding is still lacking. **Theory has made considerable progress in determining the various thermodynamic quantities via total energy calculations for certain prototype systems. For these systems, the calculations have provided a detailed understanding of the predicted growth modes, including the changeover between wetting and cluster growth.** Some of the energetic contributions, such as surface energies, can be determined more accurately and consistently theoretically than they can be measured experimentally. Since these terms are important ingredients in any understanding of the growth process, theory will play a role of ever increasing importance.

Kinetics, however, still present difficulties for first-principles methods. Needed theoretical work includes extending the calculations of the energetics to other systems, explicitly including temperature effects in both the energetics and the kinetics via first-principles molecular dynamics, and understanding how the various deposition techniques (e.g. MBE vs. electrochemical) alter the energetics and kinetics. Understanding these issues will allow the possibility of creating new, often metastable, structures and materials.

2.3.2 Interface Structure

A major challenge in the study of interface structure between two solids has been the relative paucity of suitable experimental techniques. One has often resorted to model interfaces in which one side of the interface is only a monolayer deposited on the other material in vacuum. This situation, however, has the great advantage that it models the growth process very well. The buried interface, well separated from vacuum, has only been

accessible to a few techniques, in particular MEIS/HEIS, SEXAFS, REM/TEM and XRD. Forward focusing of electrons has recently become quite valuable in this regard as well.

The vast majority of theoretical calculations of interfaces reflect the static properties of these interfaces at zero temperature. **Total-energy calculations can yield the minimum-energy configurations and the equilibrium electronic properties. They have greatly added to our understanding of, for example, band alignment and Schottky barrier formation and interface state properties. New advances required in this field include the incorporation of constituent materials with widely different properties on opposite sides of the interface, for example ionic and covalent bonding.** Another feature of real interfaces between compound materials is variable stoichiometry and interface reconstruction, for example in silicide/silicon interfaces. Theoretical schemes need to be extended or developed for interfaces between complex materials.

A multitude of interfaces has yet to be explored. One need only think of all the possible pairwise combinations of metals, alloys, semiconductors, oxides and other compounds, magnetic materials, glasses, molecular crystals, polymers, and biological materials, to realize the opportunities and challenges in this direction. Furthermore, layers sandwiched between the two sides of an interface can give rise to completely new classes of phenomena.

2.4 Advances in Established Techniques

Interplay between theory and experiment has a key role in structure determination at surfaces. The expansion of experimental capabilities resulting from the construction of new synchrotron radiation facilities will place fresh demands on theory to keep pace. Present techniques enable us to explore a wide range of surface structures and a picture emerges of complex interaction between adsorbates and substrates, frequently leading to reconstruction of the substrate.

Theoretical methods for modeling and understanding surface structure are discussed in subsection 3.2. We here concentrate on techniques that extract structural information about surfaces.

The scope of surface structure determination is intimately connected with the capabilities of the techniques used to study surfaces. A particularly stringent requirement is the ability to detect monolayer amounts of matter against the background of a bulk material. A variety of techniques have been devised that perform this under the ultra-high vacuum conditions that are needed to allow monolayer-level control of surface composition. **Many** of these **techniques utilize low-energy electrons** (10-1000 eV) as probes, which ensures high sensitivity to monolayers. A major drawback is the strong multiple scattering of electrons through the surface lattice in this energy regime, requiring careful theoretical treatment. **Much of the progress in this area involves finding better ways to handle the multiple scattering, or new ways to use electron scattering.**

An important practical consequence of multiple scattering has been the trial-and-error approach to structure determination, since direct interpretation of measured data in terms of atomic positions proved elusive until recently. Trial and error is a costly approach to structure determination, particularly for complex structures where many parameters have to be adjusted simultaneously. Notable advances are currently taking place in this area, with the introduction of the tensor LEED approach and "direct methods" in LEED.

In fact, **LEED has provided the test bed for most of the advances in the treatment**

of electron scattering at surfaces. Many of the innovations can also be used with the other techniques based on electron scattering, such as ARPES, PD, AED, SEXAFS, NEXAFS, forward focusing of electrons and electron holography. **This fertilization process is an important task for the near future, as it will greatly expand the possibilities of structural determination, especially at synchrotron radiation facilities.**

We shall thus first discuss progress in LEED in the next subsection, before turning to other electron-based techniques.

In addition, there is a number of very useful techniques based on other probes of surface structure: photons (XRD), ions (ICISS, MEIS/HEIS), high-energy electrons (REM/TEM), tunneling and forces (STM/AFM). These have also undergone notable advances, and will be discussed in subsection 2.4.3.

2.4.1 Low-Energy Electron Diffraction (LEED)

Several major innovations in the modeling of electron scattering processes have been introduced in LEED and are equally applicable to other techniques, including many that utilize synchrotron radiation.

The first is **tensor LEED**, a linear perturbation treatment of scattered intensities for structures that deviate slightly from a "reference structure". The intensity correction is rapidly calculated for many structural distortions, relative to the more costly initial full multiple scattering calculation of the intensities scattered by the undistorted reference structure. In this way, any relaxations away from a guessed structural model can rapidly be explored. It is possible to combine tensor LEED with an **automated structural search** scheme (e.g. steepest descent in terms of the R-factor that measures the misfit between experiment and calculation): this provides a **rapid determination of very complex distortions, including multilayer and adsorbate-induced relaxations.**

This concept of small perturbations from a reference also leads to the more sophisticated methodology of the **direct methods**. The validity of first-order perturbation theory allows us to directly determine the structural distortion from the change in measured intensity through a simple matrix inversion step. The procedure takes a guess at the surface structure, calculates scattered intensities for this reference structure, and relates their difference from the measured intensities to the distortion that defines the actual surface structure. Several levels of sophistication distinguish different individual direct methods.

This methodology represents a refinement of the holographic methods (discussed in subsection 2.5.2), but takes account of multiple scattering problems. Ideally we should like the straightforward holographic methods to succeed because Fourier transformation is such a delightfully simple technique. Should they fail, theorists already have in reserve the much more powerful direct methods.

As is often the case with a theoretical advance, the direct methods may extend the power of diffraction studies to new fields. Conventionally we have extracted average atomic positions from diffraction data, but the direct methods actually present us with the probability distribution of the atoms, through higher-order perturbation terms. If it happens that the atoms are in thermal equilibrium, then the probability distribution is related to the potential energy surface controlling the motion of, for example, an adsorbed atom. Few other approaches are available that can determine atomic motion in such detail, which includes vibrational, diffusional and

anharmonic motion.

Another major development has been the interpretation of **diffuse LEED, due to disordered surfaces**, in terms of local bonding geometry. Diffuse LEED has initially been applied to lattice-gas disorder for atomic and molecular adsorbates, with several results now available in this category. It has also been extended to other types of defects, such as disordered vacancies and disordered steps. This permits the structural study of more realistic models of technologically important surfaces.

Furthermore, a variety of approximations has been introduced to efficiently compute multiple scattering in complex structures. For instance, the beam-set-neglect method has allowed LEED intensity calculations for molecular overlayers with large unit cells, as well as for incommensurate overlayers. Again, such methods are also applicable to other techniques, in particular those relying on synchrotron radiation.

2.4.2 Photoelectron Techniques

The technique of angle-resolved photoelectron emission spectroscopy (ARPES) has been developed to enable the structure determination of adsorbates on surfaces, including the structural effects of the adsorbate on the substrate. The variant called angle-resolved photoelectron emission fine structure (ARPEFS) has yielded most of the structural results in recent years. ARPEFS operates at energies of 300-1000 eV, using energy-dependent intensities obtained from synchrotron radiation. Interference between the direct electron wave emitted to the detector and the indirect waves scattered from atoms near the emitter is interpreted using a multiple-scattering formalism to yield the local adsorption structure. A fixed-energy variant of ARPES has also been used extensively, in which the electron takeoff angle is varied to obtain a sufficiently large database without synchrotron radiation. Also in this case, a multiple-scattering formalism is usually necessary to interpret the data with good accuracy. In both situations, a single-scattering treatment has been applied which gives less accurate qualitative structural results.

The technique of surface extended x-ray absorption fine structure (SEXAFS) has received relatively little theoretical attention in the last decade. It is becoming clear that the Fourier-transform treatment favored for so long for the interpretation of SEXAFS data needs to be revised. **Structural results from SEXAFS data have often been in quantitative disagreement with results obtained from other techniques.** Also, multiple-scattering effects have been documented as being important in certain circumstances. A theory similar to that developed for near-edge x-ray absorption fine structure (NEXAFS) appears desirable. However, a more efficient approach is possible, since multiple scattering is intrinsically weak in SEXAFS.

2.4.3 Other Surface Structure Techniques

In the field of ion scattering for surface structure analysis, the major recent progress has occurred at low energies. **Impact collision ion scattering spectroscopy** (ICISS) has been developed to the point of providing atomic coordinates within a tenth of an Ångström by measuring shadowing cones, which are often calibrated on the same sample. The technique has been applied to surface relaxations and adsorbate-induced reconstruction, in particular. **Medium- and high-energy ion scattering** (MEIS and HEIS) have been very successfully

applied to the study of surface melting as well as interface structure, among other types of structure.

Among the synchrotron-based techniques (ARPES, SEXAFS, NEXAFS and XRD), notable developments are:

- maturation of **forward focusing** and of the interpretation of other diffraction features of emitted electrons into very attractive new tools; this includes both scanned-angle and scanned-energy studies;
- introduction of **holography**, using emitted electrons, to directly image surface structures;
- new **multiple-scattering methods** developed to better reproduce ARPES, PD and AED measurements;
- introduction of **spectromicroscopies** based on photoelectron spectroscopy and similar methods, with spatial resolution in the range of 200 Å or less.

Being largely novel techniques, forward focusing, diffraction and holography will be discussed in subsection 2.5. New multiple-scattering methods were introduced in ARPES, PD, AED, etc. because the earlier kinematic plane-wave theories often were inadequate. Multiple scattering, while being less overwhelming than in LEED, is very noticeable in angle-resolved electron spectroscopies (including the emission of Auger and inelastic electrons, as well as photoelectrons). The new calculational methods, while sharing the same basic ingredients with LEED, have adopted a cluster approach, that is more suited to the geometry of the most likely scattering paths.

X-ray diffraction has found favored application in the areas of clean metal and semiconductor reconstructions. In its standing-wave variant, XRD has also been useful to determine adsorbate positions on semiconductor surfaces. The technique has also proved very valuable for studying surface roughness. Hard-x-ray synchrotron radiation will find here an important continuing source of applications.

High-energy electron microscopy, both in the reflection mode (REM) and in the transmission mode (TEM), has been very effective at elucidating certain types of surface structure, although not with sub-Ångström resolution.

The well-established technique of **high-resolution electron energy loss spectroscopy** (HREELS) has been applied very successfully in recent years to the mapping out of phonon dispersion. Also, surface structure determination has been made possible through multiple-scattering calculations.

Atomic scattering has also been successful in phonon studies. However, this technique has been largely abandoned in detailed structural analysis, being applied more toward roughness determination, defect characterization, growth processes, etc.

Finally, we should mention here **scanning tunneling microscopy** (STM) and its relative, **atomic force microscopy** (AFM), together with the many derivatives of these techniques. Again, no sub-Ångström resolution is obtained, but the direct imaging of surface topography on the atomic scale is invaluable in many instances. Particularly useful is the ability to directly image defects and disorder, which otherwise is difficult to analyze. The promise of atom-by-atom spectroscopic and vibrational analysis illustrates the great potential of this set of techniques.

2.5 Novel Surface Structure Techniques

Several most promising new techniques have been introduced in recent years, among which we shall discuss in some detail forward focusing and holography.

2.5.1 Forward Focusing in Electron Emission

When electrons with higher energies (> 300 eV) are emitted from a surface, the dominant elastic scattering events occur in the forward direction, leading to enhanced wave amplitudes ahead of any scatterer. Outside of this forward scattering or forward focusing cone, whose position is related to a *bond direction*, are also found higher-order interference fringes that contain *bond length* information. Both aspects of these higher-energy diffraction patterns have been shown to yield useful structural information. We shall emphasize here the more recently developed forward-focusing approach.

The forward focusing of emitted electrons by atoms in their path has emerged as a very attractive new tool for surface structural study. Several processes can generate these electrons. Photoemission, Auger emission and inelastic electron collisions have all been shown to produce the desired effect of scattering the electrons into a narrow cone (of half-width around 10-15°) in the forward direction, if the electron energy exceeds about 300 eV. In this manner bond directions are directly evident as peaks in the angular distribution of electrons emitted from the surface.

Forward focusing often allows one to determine the approximate position of adatoms in a relatively straightforward manner: for instance, interstitially buried adatoms are easily differentiated from overlayer adatoms; also molecular orientations are often easily determined. In addition, the geometry of buried interfaces and of buried layers can be studied.

Theoretical analysis has revealed that multiple scattering from atom to atom plays an important role when such emitted electrons travel along a linear chain of atoms before emerging from the surface. This happens especially when studying buried atoms. Then, accurate multiple scattering calculations are necessary to assure a useful, reliable structural analysis. Also, interpreting weak peaks always requires a multiple-scattering treatment to bring out all the structural information present in the measured data.

New theoretical methods have been developed to efficiently perform the required **multiple-scattering calculations**, using in particular the cluster approach with spherical waves, rather than the slab approach with plane waves which is more appropriate at lower energies. But **these methods still need much further development to be successfully applied to more complex, interesting surface structures.**

2.5.2 Electron Holography

A very exciting recent addition to the panoply of techniques for surface structure determination is electron emission holography. Theoretical simulation and analysis play an important role in the current development of this imaging technique. The method can use various types of emitted electrons, including photoelectrons, Auger electrons and inelastic electrons.

Dennis Gabor originally proposed to do holography with electrons, but could not produce

adequately controlled electron waves due to limitations in electron optics: the method was therefore developed for photons instead. With the new electron holography, an electron wave emitted from a surface atom interferes with its own scattered waves from nearby other atoms, thereby producing a hologram on a distant macroscopic position-sensitive detector. Rather than attempt to reconstruct the image with a second electron wave (which would have to be a spherical convergent wave with sub-Ångström precision on the macroscopic scale of the detector), the image reconstruction is done in the computer, by calculating Fourier transforms.

Electron emission holography has so far produced reconstructed images with Ångström resolution parallel to the surface and less good resolution perpendicular to the surface. It has been applied to adsorbed atoms on metal surfaces, buried atoms in a semiconductor surface, clean metal surfaces, epitaxial films of metal on metal, and clean semiconductor surfaces. Compared to STM, which gives similar resolution, holography images the atomic core rather than its electronic structure, and images deeper than the topmost surface layer. On the other hand, holography only sees a restricted neighborhood of selected atoms (about a dozen neighboring atoms).

Theoretical challenges in electron holography include:

- **multiple scattering** effects, especially in the "back-scattering mode" employed with photoelectrons (it is desirable to go beyond the simple plane-wave Fourier transformation; the direct methods discussed in subsection 2.4.1 provide some answers);
- **forward scattering and multiple scattering along chains of atoms** may degrade the resolution, so that methods need to be developed to assess and circumvent this problem when the detection geometry cannot avoid it;
- the exponential decay of the forward scattering cone also degrades resolution in the reconstructed image; the continuum of energy provided by synchrotron radiation can help greatly in improving the resolution perpendicular to the surface.

3. Electronic Structure

The electronic structure of materials can be determined by a variety of photon techniques available at synchrotron radiation facilities. In particular, the most useful ones are photoemission spectroscopy in the ultraviolet (UPS) and in the x-ray range (XPS), inverse photoemission spectroscopy (IPES), x-ray absorption spectroscopy (XAS), angular-resolved photoemission spectroscopy (ARPES), Auger electron spectroscopy (AES), and electron energy-loss spectroscopy (EELS).

Electronic-structure calculations aim at the determination of the ground- and excited-state energies and wavefunction properties of the electrons in a given system. They are, by nature, many-body problems that very seldom can be solved exactly, and that require, from the start, approximate methods. These approximations are of various kinds and yield very disparate accuracies. Usually they involve either a perturbative treatment or a variational approach. The nature of the approximation also depends on whether the problem is to understand quantitatively a real or realistic system (e.g., the optical properties of the reconstructed (111) surface of silicon, the photoemission spectrum

of nickel metal, or the electronic charge distribution at a grain boundary) or to comprehend the various effects that are present in prototype, ideal models (e.g., the surface properties of jellium, the surface spectra of the face-centered-cubic Hubbard model).

3.1 Electronic Ground-State Calculations for Surfaces and Interfaces

In a real sense all physical properties of surfaces are a consequence of the electronic structure. For example, cleaving a crystal causes the electrons to rearrange at the surface. This rearrangement creates the dipole layer that, together with the chemical potential, is responsible for the work function. Furthermore, the changed charge density at the surface can cause, via electrostatic forces, relaxations and reconstructions of the surface atomic structure. Changes in the potential and boundary conditions due to the reduced symmetry at the surface can cause electron states to become localized surface states or resonances which affect properties such as conductivity and adsorption.

Many of the electronic properties are probed by various spectroscopic techniques such as photoemission, inverse photoemission, core-level spectroscopy (XPS, AES, EELS, and AES). **These methods all have the common feature that they do not directly measure the ground state, but rather specific excited states of the system.** Since it is the ground state that is often of interest in determining the bonding and mechanical properties, it is necessary to be able to relate the measured quantities to the ground state. **The framework used to describe most experiments and physical properties is the single-particle picture.** This picture provides a physically appealing and intuitive way to understand the properties of the real system, even when many-body effects may also be important.

Density-functional theory provides one such a framework. This method converts the many-electron problem into a set of equivalent one-electron problems in an effective potential. Since the exact exchange-correlation functional is not known, approximations such as the local density approximation (LDA) are needed in order to do quantitative calculations of models of real systems.

The present generation of methods for solving the LDA equations differ in the detailed approximations used for the potential and the single-particle wavefunctions. The choice of method depends in large part on the questions being asked. For example, a simple method that can solve the LDA equations for many particles that includes the surroundings with only fair accuracy may provide a better model and understanding of the system than a more precise solution of only a few atoms. Methods that treat the surface as either a finite film or as a repeated supercell are currently limited to unit cells of approximately 20-50 atoms. For many local properties these models are adequate since the screening length (at least for metals) is on the order of a lattice spacing. For questions such as those related to transport properties, where a correct coupling to the bulk continuum is necessary, method using Green's functions are often employed. Questions concerning long-range interactions or phase transitions are beyond the capabilities of today's methods and computer resources.

Ground-state surface properties that can be calculated today include the atomic structure (relaxations/reconstructions), adsorbate vibrational frequencies, surface energies, and adsorption energies. Many of the calculated thermodynamical quantities are either inaccessible to experiment, because they correspond to metastable (or unstable) states,

or else they are so difficult to measure that from a practical point of view they are unknown.

In addition to the energetics, a whole class of questions related to spectroscopy can be addressed. For systems in which single-particle and self-energy effects are small, **the calculated LDA surface band structures can give valuable information concerning the location, dispersion, character, and consequences of surface states and resonances.** For example, surface states are known to be the driving mechanism for certain surface reconstructions and relaxations, as well as providing chemically active sites for surface reactions. The detailed microscopic understanding of the origin of surface states and changes caused by adsorption is largely due to surface band-structure calculations.

Core-level spectroscopies are often used to infer information about changes in bonding and charge transfer at surfaces. Comparisons between calculated and measured core level shifts provide a bridge between simple models and the real systems. Detailed calculations are particularly important in helping to build physical intuition and differentiating between possible plausible models. Although core level shifts, for example, are now reasonably well understood, questions of how the contributions to the core level lifetimes caused by phonons and other processes at surfaces differ from those in the bulk are not.

For many interesting and technologically important materials, the single-particle LDA results are not adequate to describe the measured spectroscopic data such as photoemission spectra. For systems with stronger correlations, many-body effects cause significant distortions of the single-particle spectra. **To understand these experiments, many-body effects must be included.**

The needs and challenges in surface electronics over the next few years can be divided into two broad categories: 1) computational techniques and 2) advances in basic theory with applications. The advances in computational techniques will include solving the standard surface electronic structure faster and for larger systems in order to make more realistic models; better representation of the coupling of the bulk continuum to the surface; treatment of impurities and disorder on the surface (real surfaces and interfaces have disorder and have impurities present); and the first-principles treatment of thermal and dynamical effects on surfaces requiring methods capable of treating thousands of atoms. Although these advances all involve difficult technical problems, significant progress has already been made.

The questions of advances in basic theory relate more to the treatment of excited-state properties and the relationship to experimental data. The inclusion of correlations on the same footing as the single-particle terms is a difficult problem. Although there have been some significant advances in this direction, much more work is still needed in order to treat more realistic systems. As an example, are the correlations (Hubbard U) different at the surface than in the bulk and what will be the effect of such differences? Can experiments such as photoemission or Auger spectroscopy determine these quantities? What physical pictures can be used to relate the experiments to the ground state of the material? As important as a detailed microscopic understanding is, there is also a need for more "macroscopic" theory on such topics as phase transitions and melting at surfaces.

3.1.1 Fermi-Surface Effects and High-Resolution Photoemission

Until now, most of the ARPES experiments have been done with energy resolution larger than 100 meV. Today, using low-emittance machines and undulators, it is possible to expect 10

meV with a 10° angle resolution. With the future ALS one can expect to reach a resolution of just a few meV. Why is that important? Because, very often, the most interesting information to be obtained comes from states that are very close to the Fermi level, i.e., within 200 meV. Recent observations of the opening of the superconducting gap in the high-temperature superconductors with good resolution (32 meV in ARPES; 13 meV in integrated photoemission) show the exceptional capability of this technique.

One should be able to study many exotic systems, such as the Kondo effect, Peierls transitions, organic superconductors, classical superconductors, and, in particular, look at the difference in the band structure when the materials have a transition from the normal to the superconducting state. Electronic-structure calculations must, therefore, achieve an accuracy compatible with the soon-available experimental tools.

3.1.2 One-Electron Problems Caused by the Lack of Periodicity

Understanding of the physical and mechanical properties of materials hinges crucially upon the ability to determine the electronic structure of systems containing defects with two-dimensional periodicity. It is well known that properties such as corrosion, catalytic activity, embrittlement, and others are intimately connected with the electronic behavior of surfaces and interfaces, e.g., grain boundaries. The presence of defects with even lower symmetry, dislocations for example, may require the treatment of structures such as lines and corners of atoms. Because these defects are not characterized by full translational periodicity, conventional electronic-structure methods which are based on the presence of translational invariance and Bloch's theorem cannot be used for their treatment without approximations, often severe, to the physical underlying structure. Thus slabs, repeating slabs, and repeating supercells are often employed in attempts to determine the electronic structure of surfaces and interfaces. Perhaps the most successful approach to the treatment of surfaces and coherent interfaces is that of layer doubling. However, although such methods can often yield meaningful results, they do not allow a fully satisfactory treatment of the semi-infinite nature of many important systems.

In order to provide a proper treatment of the boundary conditions associated with systems with broken translational invariance, it is necessary to seek methods that do not rely on the concepts of reciprocal space and on the validity of Bloch's theorem. Such methods can in fact be founded upon a very simple property of systems with two-dimensional periodicity and of infinite extent. Consider a surface as consisting of a plane of atoms, or sets of planes of atoms, that repeat periodically in a direction perpendicular to and away from the surface. These repeating planes or stacks of planes can be labelled "repeating units". It is clear that the properties of the system do not change when an integral number of repeating units is removed from the free end of the system. This removal-invariance property of systems with semi-infinite periodicity (SIP) allows one to obtain the Green function, and hence all single-particle properties, of any system with SIP, such as surfaces and interfaces. Even corners of atoms, such as a quadrant of a monolayer or a three-dimensional corner, can be treated using this technique. To see this, it suffices to visualize a two-dimensional corner as the periodic repetition of a half-line, or a three-dimensional corner (in the case of a simple-cubic structure) as the periodic repetition of a quadrant of a monolayer. **By replacing the concept of translational invariance**

with that of SIP, and Bloch's theorem by the principle of removal invariance, one can provide an exact treatment of many low-symmetry systems, in particular of surfaces, grain boundaries, and dislocations.

These new methods allow, in many cases for the first time, the accurate study of the electronic structure of heterogeneous and incommensurable interfaces, of adsorbed and absorbed atoms and molecules and other systems of physical and technological importance. Initial applications of these methods have been made to elemental Cu and Nb containing twist and tilt grain boundaries, and to dislocations in Cu. Further development, currently in progress, is aimed at extending the present stage of the codes to include the calculation of charge self-consistency and of total energies.

3.1.3 One-Electron Interference Phenomena at Overlayers

Thin layers of epitaxial growth have a unique electronic structure which is reflected in their transport properties and atomic structure. Photoemitted electrons travel only a few Ångströms, but the **hole states** left behind **can have very long mean free paths**: holes in the *sp* band of noble metals and near the top of semiconductor valence bands may travel as far as 200 Å and act as sensitive probes of the overlayer/substrate interface.

A calculation was made of the photocurrent from 7 monolayers of silver on palladium. Sharp peaks occur which are due to the resonances established between the front and back surfaces of the film. Their amplitude and position in energy give the reflection coefficient of the interface. The spacing between peaks gives the group velocity of the band, dE/dk. The peak spacing closes up as broad *sp* bands give way to *d* bands at around 3 eV (approximately 0.1 Hartree). The energy range 3 to 7 eV (0.1 to 0.25 Hartree) corresponds to a band gap of palladium where the interface reflectivity must be large, and intense narrow peaks are seen. At higher energies holes can escape into the palladium and less intense structure is seen.

Observation of these dramatic effects is a sensitive monitor of the perfection of the films: fluctuations in thickness, for example, will destroy the fine structure. **Given near-perfect films, a rich haul of information can be had concerning electronic and magnetic properties of thin films.**

3.1.4 Alloys

The study of surfaces and interfaces **in disordered substitutional alloys** affords challenges that often overshadow those associated with pure materials or ordered alloys and compounds. Not only does one have to deal with the loss of translational invariance in directions perpendicular to the surface or the interface, but **the statistical nature of the problem presents new difficulties**. One approach in determining the electronic structure of disordered-alloy surfaces and interfaces is to extend familiar concepts, such as that of the coherent potential approximation (CPA). Cluster techniques and direct configurational averaging can also often be used to advantage. It is also formally possible, although it has not yet been implemented, to combine the concepts of the CPA with those of the real-space methods developed for the treatment of systems with SIP (see subsection 3.1.2). Using these methods, **it is possible to obtain information about such important physical properties as surface segregation profiles and interdiffusion.**

3.2 Total Energy Calculations

There have been considerable successes in the past decade, using total-energy methods, in verifying and predicting structural and bonding properties of surfaces and interfaces. In these studies, the structure is determined by minimizing the total energy with respect to the atomic coordinates or, equivalently, by searching for zero-force structures. Additional valuable information, including the nature of the chemical bonds and the vibrational properties of the system, is obtained.

A number of theoretical methods are being used, ranging from first-principles approaches such as the LDA formalism and quantum-chemistry methods to semi-empirical tight-binding techniques and the classical valence force field methods (with pair- and many-body potentials). **The first-principles calculations such as those based on the LDA have given very accurate results on surface structures, vibrational modes and binding energies for systems with moderate numbers of atoms in the surface unit cell. The more empirical approaches have provided insights and semi-quantitative results for a host of more complex systems. A very encouraging recent development is the possibility of combining total-energy calculations with molecular-dynamics techniques in the so-called Car-Parinello method.** This latter approach treats the electronic and atomic degrees of freedom simultaneously and thus provides a way to calculate the dynamical and thermodynamical properties of surfaces and interfaces in addition to the quasi-static properties.

3.3 Quasi-Particles, Low-Lying Excited States, and Optical Properties of Surfaces and Interfaces

An effective way of probing the electronic structure of a system is by examining its electronic excitation spectra by means of spectroscopic techniques such as photoemission, optical, and various energy-loss spectroscopies. Photoemission techniques, as discussed in subsection 3.1.1, have been extremely fruitful in the study of surfaces. Results from optical measurements are slightly more difficult to interpret. However, optical techniques such as differential reflectivity and second harmonic generation have the added advantages of being highly nondestructive and applicable to solid/solid and solid/liquid interfaces, in addition to surfaces.

However, unlike the structure and related ground-state properties, **the excitation spectra of surfaces and interfaces constitute an area which until recently has not been subject to detailed quantitative calculations.** Empirical methods based on bulk parameters in general are not accurate because of the changes in environment at the interface. Traditional *ab initio* one-electron approaches based on ground-state theories (e.g., LDA or Hartree-Fock) have also proven inadequate. For example, as in the case of bulk crystals, LDA calculations inevitably underestimate the band gaps between the occupied and empty surface states, typically by 50% or more. This discrepancy arises because **the interpretation of electron excitation spectra requires the concept of quasi-particles**, the particle-like excitations in an otherwise strongly interacting electron system. **Owing to electron-electron interactions, the properties of the electron are renormalized from those of one-electron theories, giving rise to different energies, effective masses and finite lifetimes.**

The recent development of a self-energy quasi-particle approach now allows

first-principles calculation of electronic excitation spectra. Highly accurate results (e.g., surface-state energies in agreement with experiment to within 0.1 eV) have been obtained by including local-field screening and dynamical renormalization effects in the electron self-energy. Successful applications have been made to the optical, energy loss, and photoemission spectra of semiconductor surfaces, interfaces, and superlattices. Further, **the accuracy of these calculations has made possible the use of the computed results as a basis for investigating new effects such as electron-hole and electron-lattice interactions in the optical excitation process.**

Synchrotron radiation facilities like the ALS should be ideal for studying the electronic structure of surfaces and interfaces. With photons tunable over a broad range of frequencies, the optical and photoemission properties for many systems – including clean surfaces, atomic and molecular adsorbate systems, semiconductor-metal interfaces and semiconductor-insulator interfaces – could be investigated in great detail. The time structure of the beam would also allow the study of the dynamics of the excited carriers at the interfaces. Quasi-particle calculations of the kind described here should be invaluable in the interpretation of the wealth of data anticipated from these experiments.

3.4 Many-Body Effects

There are many electronic effects that depend, not on the one-electron properties of solids, but on the detailed correlations that the electrons have among themselves. When these effects are overwhelming, the results are such that the condensed-matter system resembles strongly a collection of quasi-independent molecules, weakly bound by residual (Van der Waals) forces. The problem can therefore be tackled theoretically with the tools of atomic and molecular physics.

The problem is much more complicated when the system is metallic, but with **strong electron-electron correlation effects**. These systems include **transition metals, rare earths, and actinides, as well as their compounds.** The resulting effects are as varied as **strong ferromagnets and antiferromagnets, ferrimagnets, charge- and spin-density-wave systems, mixed- and intermediate-valence systems, heavy fermions, etc**. Nickel metal is a typical, albeit relatively simple, system.

Nickel metal has a very narrow one-electron d-band width (4.3 eV according to reliable band-structure calculations) and a considerably strong intra-atomic electron-electron interaction, estimated to be between 2.5 and 4.5 eV. It is therefore a very strongly correlated transition metal. Its photoemission spectrum exhibits many interesting features and has been the subject of numerous theoretical contributions. In particular three features require special attention, because they cannot be explained based solely on one-electron band-structure effects:

- there are satellites in core-level photoemission spectra, approximately 6 eV below the main lines;
- resonance photoemission was observed at 67 eV photon energies (the $3p$ to $3d$ transition) for a satellite approximately 6 eV below the Fermi level;
- valence-band photoemission shows an apparent d-band width reduced by 25% and an exchange splitting reduced by 50% from the values obtained from band-structure calculations.

This problem is ideal for treatment by the so-called **small-cluster approach**. It consists of including only a small cluster of N atoms with *periodic boundary conditions*, which is equivalent to sampling reciprocal space at a well-defined finite set of N points. Within this restricted set the problem is solved exactly, with one-electron and many-body effects treated simultaneously and on equal footing. It has thus been studied, in the four-atom tetrahedral approximation of the fcc lattice (the crystal structure of Ni metal), including ten electron orbitals per site, the one-electron energy parameters of Wang and Callaway, and full intra-atomic electron-electron interactions between the various d-orbital electrons. Atomic symmetry allows for three independent intra-atomic interaction parameters, normally labelled U, J, and ΔJ, which have been kept in the ratio 56:8:1, and scaled to provide the proper satellite spectral position. A value of $U = 4.3$ eV yields the best results.

The cluster consisting of 4 sites contains 40 d-orbitals; 38 electrons (2 holes) were included in the ground state, yielding an average occupancy of 9.5 d-electrons per atom, very close to the observed value of 9.46. The ground state of the system can be obtained analytically and in closed form. It has a well defined symmetry ($^3X_2$) and is ferromagnetic. Because of the Pauli exclusion principle it has zero probability of having two holes in one site: the holes are (through exchange) perfectly correlated with one another, and consequently, counting from the full d-shell, there is no contribution to the ground-state energy from the one-site, hole-hole interaction.

The photoemission process introduces a third hole into the system. The three-hole manifold of the tetrahedral cluster contains 9880 many-body states. The use of group theory simplifies the matrix considerably. The photoemission spectrum is obtained by projecting the $^3X_2$-ground-state with an extra hole into the three-hole energy-eigenvalue spectrum. By selecting the desired one-electron-orbital **k**-vector, space and spin symmetries of the extra hole (the photoemitted electron), angular resolution (only for **k**-vectors at Γ and X), spin polarization and spatial distribution spectra can be determined.

The discrete spectrum of 9880 lines, broadened with a narrow Gaussian of 0.15 eV half-width, compares well with experiment not only in the existence of a satellite, but in its relative intensity with respect to the main band of the spectrum. Analysis of the *complete spectrum* within the four-atom cluster shows that states near the Fermi level are characterized by single, narrow peaks with essentially no satellite strength. States near the bottom of the band have strong satellite components and exhibit a well-known atomic-like multiplet structure.

The results yield the following conclusions:

- three-hole eigenstates corresponding to the "main band" have a greatly reduced probability of finding two holes in the same atom (20% at the Fermi level, 5% at the bottom of the band), as opposed to 50% in a random state created from the ferromagnetic $^3X_2$ ground state;

- three-hole eigenstates in the satellite part of the spectrum have a very high probability of finding two holes in one atom;

- the many-body calculation yields a considerably reduced bandwidth of 3.4 eV, in excellent agreement with the experimental value of 3.3 eV, and considerably reduced from the band-structure value of 4.3 eV;

- band-structure calculations yield a Fermi-level (X_5) line which consists only of majority-spin electrons – the corresponding minority-spin states are above the Fermi level, i.e. empty; the results of the many-body small-cluster calculation indicate that the X_5 Fermi-level line is a combination of both spins, that the minority states are appreciably occupied in the true many-body states, and that the exchange splitting of that X_5 level is very small;

- agreement with experimentally determined values of the spectral lines is very good throughout, with the exception – similar to previous work – of the energy of the assigned X_2 symmetry.

This procedure has been extended to several other systems, with other elements (Cr, Fe, Co, Ni, Cu) and other model hamiltonians (Hubbard systems, heavy fermions, superconductors, alloys, etc.) and to a variety of geometries (fcc and bcc cubic systems, tetragonal systems, freely standing thin layers of one, two and four atoms). It offers **great promise to study the photoemission spectra of systems which are metallic and strongly correlated. The results thus far indicate that under those circumstances the effect of the environment and of the one-electron potentials tend to be magnified and enriched by the strong but delicate many-body effects.**

3.5 Magnetic Properties of Surfaces and Interfaces

3.5.1 Magnetic Structure of Surfaces, Thin Films, Interfaces and Overlayers

Ab initio **techniques based on the one-electron local spin-density approximation have recently been very successful in predicting trends in magnetic properties in a variety of systems; they need, however, to be applied** – as resources and computer capabilities permit – **to a wider variety of magnetic-surface and thin-film systems.** Details of surface magnetic properties which depend on the lowered symmetry require techniques which explicitly represent the solid-vacuum interface by means of boundary conditions on the electron wave functions or density – the so-called film codes. These calculations are extremely time-consuming and expensive, and the codes are in use at only very few places.

Magnetic properties of interfaces between two different materials, which also involve lowered symmetry, can be simulated either by film codes or by layered supercell calculations which use bulk codes. In either type of calculation the spatial scale of properties which can be investigated is limited by the number of atomic layers which can be included in a unit cell, currently of the order of 10. For example, investigation of the very interesting coupling observed between Fe layers in Fe/Cr/Fe sandwiches and Fe/Cr superlattices, which occurs for Cr thicknesses of 10-20 Å, will require a very large expenditure of state-of-the-art supercomputer time.

Structural relaxation at surfaces and interfaces makes the limitations of supercomputer resources even more acute, as the existence of such relaxations requires significantly larger unit cells. In addition, if structural relaxations are not known, calculations of many different structural configurations may be required in order to determine the minimum-energy relaxation.

The total-energy capabilities of *ab initio* calculations can be used in a different way to predict magnetic properties of thin films which are caused not by the lowered symmetry but rather by strain or lattice distortions due to interface bonding. Bulk codes have proved to be very successful in predicting the systematics of magnetic structure – nonmagnetic versus

ferromagnetic versus antiferromagnetic arrangements – as a function of lattice parameters and lattice symmetry. Calculations have been performed for most of the $3d$ magnetic transition metals in the bcc and fcc structures. However, hexagonal and lower-symmetry structures – e.g., tetrahedrally, orthorhombically, or trigonally distorted bcc and fcc systems – are just beginning to be investigated.

In addition to the *ab initio* calculations, which are involved, expensive, and require state-of-the-art supercomputers, there is an obvious need to develop simpler correlations and empirical rules which could either provide qualitative explanations for existing experimental data on magnetic properties or point toward systems and configurations which might exhibit some required magnetic property.

Beyond the calculations of equilibrium structures and primary magnetic properties (magnetic moment, hyperfine field, exchange splitting, etc.), **there is a crucial need to determine secondary magnetic properties, such as anisotropy and magnetostriction, by means of electronic-structure techniques.**

Finally, the richness in structure and the complexity of the magnetic systems are a source of surprises for new, unexpected, unexplained, or misunderstood effects which require both qualitative and quantitative explanation. Theory can develop only by the simultaneous paths of constant interaction between theory and experiment, and by the formulation of (by necessity) simple models to extract, from the large number of secondary and irrelevant effects, the basic features of the particular phenomenon under consideration.

3.5.2 Magnetic Moments at Surfaces and Interfaces

The values of the moments at the surface of magnetic metals remain a lively issue which needs more careful experimental data. All theoretical calculations agree with the fact that at free surfaces the magnetic moments tend to be enhanced (in weakly magnetic metals) or created (in almost magnetic metals), even though the precise values of those moments tend to vary appreciably from calculation to calculation. The available experimental data, although not fully in agreement with each other, tend to confirm indirectly these theoretical predictions. Experimental confirmation, with direct experimental measurement of the specific surface and/or interface moments, is not yet available.

For example, **several issues require further clarification, theoretical study, and reliable experimental data:**

- the repeatedly calculated and indirectly observed (by photoemission studies) **large magnetic moment at the (001) surfaces of antiferromagnetic chromium** – a ferromagnetic layer in an ideal, defect-free surface – remains yet to be observed directly;
- optically observed **dead layers of iron (201) when deposited on ruthenium (0001)** remains a puzzling effect which requires careful theoretical and experimental work; an accurate self-consistent calculation, including structural rearrangement effects, and the performance of the experiment at low temperatures is needed;
- **the magnetic moments, if any, of the free surface of vanadium and of vanadium overlayers** on a variety of substrates remain an open question.

These are only a few examples of systems which remain to be examined; the general area is still only sketchily explored and is a rich ground for basic theoretical and experimental research with possibly many practical applications.

3.5.3 Magnetic Coupling at Interfaces

One of the most exciting areas of both current and future research is that of **coupled magnetic multilayered systems**. In the simplest case, materials engineering of these magnetic systems allows for the optimization and control of such basic magnetic properties as saturation magnetization, anisotropy, coercivity, and magnetic domain structure. **Distinctly new properties of coupled magnetic systems have recently been discovered in a number of different magnetic materials.** The most recent discovery is that of antiferromagnetic coupling of neighboring Fe layers in Fe/Cr/Fe sandwiches.

Examples of **areas of research likely to produce important new results include**:

- a **search for new ferromagnetic/metal/ferromagnetic layered structures** for displaying antiferromagnetic coupling of ferromagnetic layers;
- **non-equilibrium spin injection and removal in ferromagnetic/metal/ferromagnetic structures**, and in particular the magnitude of the spin polarization propagated across the ferromagnetic/metal interface;
- study of **ultra-thin layers deposited on top of ferromagnetic, antiferromagnetic substrates.**

4. Chemical Reactions and Dynamics

The field of chemical surface reactions and dynamics is rich and varied. It includes **heterogeneous catalysis, surface space charge effects, corrosion, crystal growth and epitaxy, evaporation, tribology and its many mechanical processes, like friction, lubrication and surface hardening.** The range of theoretical problems is equally wide. Due to the dynamical nature of these phenomena, their theoretical description is in many ways not as advanced as it is in the fields described in previous sections, which tend to refer to static properties of surfaces. **Phenomena whose dynamics figure prominently in important surface processes include**:

- evaporation;
- crystal growth;
- surface disorder;
- transient phenomena;
- events that are controlled by small energy differences;
- order-disorder and other phase transformations;

- adsorbate-induced restructuring;
- restructuring at rough surfaces;
- photon-surface, electron-surface, ion-surface and atom-surface interactions;
- lubrication, wear and other tribological processes.

Much progress has been achieved in several areas related to surface chemistry and dynamics; for example:

- characterization of atomic and molecular adsorbate structures;
- investigation of factors governing activation of simple chemical reactions by metal surfaces;
- elucidation of elementary steps and kinetics controlling a number of basic surface reactions;
- detailed measurement and theoretical investigation of surface diffusion by atomic and small molecular adsorbates;
- understanding of the effects of promoters and poisons on simple reactions;
- clarification of the character and effect of lateral interactions on surface processes.

While these fundamental processes are essential elements in understanding more complex surface reactions, **a number of other issues remain unclear, such as:**

- **role of surface reconstruction in modifying reactions and dynamical processes;**
- **mechanisms by which surface defects, steps, disorder, and other forms of surface roughness affect catalytic reactivity and selectivity;**
- **origins of structure sensitivity in surface reactions;**
- **factors controlling the relative importance of ensemble or long-range electronic effects on reactions and dynamics;**
- **fundamental mechanisms in most areas of tribology, from adhesion to crack propagation.**

Most of the phenomena that have been listed above are best addressed under controlled surface conditions using ideal materials. Clearly much work remains to be done here. **A major challenge for the next decade**, however, **will be to move beyond idealizations in the direction of more realistic models** of catalytic chemistries and tribological systems. Such an effort will require close interaction between theorists and experimentalists, as methodologies for achieving such advances are only beginning to become available.

Investigations should be performed in parallel both on the fundamental processes at idealized surfaces and on new approaches to characterize more realistic reaction systems. We describe in the following subsections some of the significant challenges facing surface research. Topics have

been ordered from the most fundamental and microscopic processes to those which directly address the technologies motivating the basic science. We give particular emphasis to the role that synchrotron-based experimental methods can play in these developments and to the theoretical developments that will be necessary to meet these challenges.

4.1 Dynamical Processes on Surfaces

Adsorbate and surface dynamics play an essential role in the kinetics of both physical transformations (annealing, crystal growth, reconstruction and phase transitions) and many chemical reactions at surfaces. While a number of experimental techniques have provided measurements of spatially averaged mobilities for a variety of atoms and small molecules, little is known about the detailed microscopic dynamics of surface diffusion, because of the experimental difficulties in probing such dynamics at sub-micron distances. In order to advance our understanding of the role played by surface transport in chemical reactions, we have to obtain at least the same level of information on the dynamics of adsorbed molecular species and reactive fragments, which field emission techniques (FIM, FEM) have obtained for atomic diffusion on metal surfaces. This information is required not only for isolated species, but also for concentrated physisorbed and chemisorbed adlayers in which lateral interactions often play a major role.

Very recent experimental advances in surface spectroscopies are highly encouraging with regard to studying microscopic mobilities of molecular species. Both second-harmonic generation (SHG) and surface infra-red spectroscopy (SIRS) have chemical specificity (even mode-selectivity for SIRS), and both are amenable to the fluctuation techniques used successfully in FEM to obtain diffusion coefficients for strongly interacting systems at high concentrations. Thus with the opportunities which the synchrotron radiation facilities offer for improvement of both spatial and time resolution, there will be a whole new class of complex molecules, and possibly also reactive intermediates, whose surface mobilities will be measurable at a microscopic scale. Because of the large range of time scales potentially available, the influence of these facilities will probably be even greater in this area than that of STM, which can provide the most microscopic spatial information, but which has quite limited time resolution capabilities.

Such **advances in experimental capabilities will require major developments in our theoretical treatments of surface dynamics.** Because of the large time scale differences between long-range (diffusional) adsorbate and surface atom motions, previous theoretical treatment of surface mobilities have largely been restricted to consideration of the individual jump processes between sites. However, diffusion of light particles can involve long-range transfers, as is well known for hydrogen where strong quantum effects are also evident. Furthermore, the effects of excitation of internal degrees of freedom for molecular adsorbates is an important aspect of dynamics of more complex species, which has not been considered at all so far.

Other issues which will require consideration as our expertise in handling the dynamics increases, include the effects of defects, steps, and extensive surface atom participation in the adsorbate dynamics. One of the most challenging problems for theory is how to develop techniques for solving the nuclear dynamics (with their own often disparate time scales), when the electronic structure is strongly dependent on the nuclear configurations. Some theoretical work addressing this is underway for metal atoms on metals, but much more effort is needed in this direction. The possibilities of self-consistent molecular

dynamics/electronic structure algorithms like that of Car and Parinello would be very useful to explore here, both for the response of the surface electronic and of the surface vibrational degrees of freedom.

Finally, with the exception of quantum diffusion of hydrogen, there has been virtually no theoretical effort beyond use of lattice gas models, in the development of microscopic dynamical theory for interacting adsorbates at high concentrations. Obtaining experimental information on this for the first time from the new facilities will be crucial in stimulating theoretical progress in this challenging and chemically relevant regime.

4.2 Elementary Surface Reactions

Studies of surface reactions in the last decade have pursued both the characterization of static adsorbate properties (particularly molecular adsorbate structures and thermodynamics), as well as the activation of molecular bonds by metal surfaces (including dissociative adsorption and reactions of adsorbed species). Static properties are crucial to determining surface reaction mechanisms, since ultimately it is the relative thermodynamic properties of reactants, potential intermediates, and products that determine which reaction pathways even merit consideration.

The simplest elements of bond activation by surfaces are relatively well understood at this point. Various mechanisms by which the surface participates have been explored; such mechanisms include providing **a high density of states at the reaction site, a polarizable substrate, and unoccupied states near the Fermi level.** While this establishes a simple framework for conceptualizing the process, a great deal remains to be determined. **Global variations, such as trends in activation energetics for a given reaction among different transition metal substrates are not well understood.** Similarly, **electronic variations**, such as the relative importance of covalent, ionic (i.e. heterolytic) or charge-transfer bond-breaking processes under different surface conditions, **are unclear**. More specific questions include the role of tunneling in facilitating bond breaking in reactions with high barriers (e.g. C–H activation), or precursor states in dissociative adsorption.

Elucidating elementary reaction steps gives rise to great theoretical and experimental challenges. Experimentally, the species of most critical interest are reaction intermediates which typically have short lifetimes and low concentrations and are thus difficult to detect. Time-resolved infrared reflection absorption spectroscopy (IRAS), or near-edge x-ray absorption fine structure (NEXAFS) experiments represent frontier areas where progress could substantially improve understanding.

Theoretical studies of molecular adsorbate properties and bond activation are hampered by the fact that species of similar stability are common on surfaces and activation energies are usually low, thus requiring a high degree of accuracy for convincing comparisons of possible pathways. Traditionally, metal clusters have been employed as bulk surface models in studies of molecular adsorbates, but the needed accuracy has rarely been achieved. More recently, treatments of surface reactions using semi-infinite slab models have been carried out in which the reaction is repeated periodically on the surface. **Clearly, substantial challenges remain in the development of theoretical methods to obtain generally valid approaches.**

4.3 Surface Structural Effects on Chemical Reactions

A standard assumption in surface chemistry studies has been that most ordered metal surfaces retain their order during surface reactions. There is ample indirect evidence that this assumption is at times violated, perhaps frequently so. Examples of surface restructuring due to atomic or molecular adsorption are common. Correlations between reaction rate and surface roughness (e.g. as implied by high Miller indices) have been established. Abrupt changes in reaction rate as a function of temperature have been observed, implying that an adsorbate-induced surface phase transition may have occurred that enhances (or inhibits) the reaction.

Such questions are intimately related to catalyst performance, where surface inhomogeneities are common and recognized as an important performance variable. Exactly what role surface roughness or transformations might play during a reaction is unknown, however. It has long been suggested that metal atoms at steps or kinks on surfaces, by virtue of their change in coordination, might provide modified electron density which facilitate particular reactions. Alternatively, the low coordination of edge sites may lead to reduced non-bonded repulsions between surface and reactant, thus providing lower activation barriers and greater reaction rates. Recently, it has been suggested that surface phase transformations might be inextricably coupled to the overall thermodynamics or kinetics of the reaction and not be unique to surface defects. In such a model, surface reactants are best thought of as an aggregation of both the adsorbates and the metal atoms at the reaction site . If such arguments are correct, one would have to accept that the perfect surfaces generally assumed to be present in surface reactions, in fact rarely exist, and in any event, are poor models on which to base conceptual views of surface reactions.

The experimental and theoretical testing of such notions is particularly challenging. To the extent that surface restructuring is accompanied by detectable changes in surface electronic structure, synchrotron-based microscopies that employ contrasting methods can be used. Work function contrasting has been used for example to monitor CO oxidation on Pt (an oscillatory reaction) where adsorbate-induced restructuring is presumed to occur. Time-resolved structural probes (such as SEXAFS) are not presently available, but would be invaluable for pursuing this question. Theoretical investigation of such a question would require a substantial degree of development. **Total-energy calculations that can address reacting molecular adsorbates in the presence of a changing substrate geometry do not exist.** The Embedded Atom Method has been used to explore substrate rearrangements of this complexity, but in the absence of molecular adsorbates. Extensions of this method to include covalent bond-breaking processes are under development, and may provide a means of probing this question.

4.4 Materials Effects on Surface Reactions

The importance of substrate modifications in controlling reactions on surfaces is at the very heart of modern catalysis. **Despite its importance and much research, systematic understanding of how changes in materials control the chemistry is largely lacking.**

Advanced characterization methods, in combination with theory, do provide opportunities for improving this situation, however. EXAFS is an essential technique in this regard, but it can now be complemented with a variety of microscopy techniques. XPS Imaging

is particularly attractive as a means of identifying elemental distributions and chemical states in complex catalytic materials. With such information it becomes possible to construct theoretical models of catalytic materials and to qualitatively address variations in surface chemistry that might be associated with materials variation. Because of the low symmetry and complex composition of most commercial catalysts, first-principles models of such materials are unlikely to be available. Such materials likely can be modeled using semi-empirical methods, however, given solid experimental guidance as to definition of the model. With such models, we can hope to gain qualitative information as to the effect of materials constituents on electronic properties of the catalyst and their effect on reactivity.

Simpler models of materials effects are possible both theoretically and experimentally. Models of catalyst promoters (such as alkalis) have been studied experimentally and theoretically for some time. Models suggesting that such promoters operate by modifying the density of states near the Fermi level have been proposed. NEXAFS studies of thio compounds on molybdenum disulfide catalysts have been carried out in conjunction with theoretical modeling. Detailed compositions of alloys and promoted metal substrates can be determined and can presently be modeled at least crudely. Particularly exciting are recent advances in producing monodispersed metal cluster sources that can be deposited on "inert" substrates, providing a well-characterized route to supported catalyst models. Early examples of such systems have already been characterized via XPS.

Model materials such as these can, in certain instances, be examined using conventional solid-state theoretical techniques. For the more structurally complex materials (such as supported clusters), effective medium methods may ultimately be extended to consider reacting systems in such a way as to permit a wide range of materials investigations.

4.5 Simulation of Complex Surface Reaction Networks

Virtually every surface chemistry process of interest requires multiple steps to reach a desired product. Typically, in determining the mechanism, many more competing steps require consideration. **For processes of commercial interest, reaction networks involving tens or hundreds of potentially competing steps are not uncommon. A key challenge facing surface chemistry is the development of reliable phenomenological or analytic models capable of screening the myriad possible steps in a reaction in order to focus on those few that are rate-limiting or merit further attention.** Numerous attempts to develop such approaches have been made in the past, but the paucity of experimental data with which to refine the models and the absence of a sound conceptual basis have limited success.

Improvements in both data availability and conceptual framework have improved the prospects for this type of model in recent years. The Bond-Order Conservation (BOC) model has been used successfully to examine CO methanation chemistry on several metal surfaces, and is able to reproduce a wide range of other available experimental data from within a relatively simple framework. Substantial efforts remain necessary however to validate both the conceptual framework and predictive ability of this modeling approach.

4.6 Applications to Catalysis, Combustion, Tribology and Electrochemistry

Traditionally, research in surface chemistry has been intended to ultimately provide impact on catalysis research. While this need remains a central motivation, there are other technological areas where surface chemistry research can play a role. An example is the study of tribology, which encompasses a wide variety of mechanical surface and interface processes: friction, lubrication, wear, adhesion, fracture, crack formation and propagation, surface passivation and hardening. Other examples include corrosion and surface chemistry under combustion conditions.

On an atomistic scale, processes like **friction** and **wear** are manifest via the creation of surface defects, the breaking of surface bonds, and a variety of possible high-pressure and high-temperature surface reactions. Considerable parallels may well exist between catalytic reactions and those reactions that are induced during friction and **corrosion** chemistry. The processes by which metal surfaces may be protected against these degrading chemistries are amenable to surface science investigation. The use of alloys or film forming **lubricants** and **additives** to control corrosion and wear is common, yet the detailed mechanism by which these protectants perform has not been investigated on a microscopic scale even under ideal conditions, and certainly not under normal operating conditions.

Surface chemistry under combustion chamber conditions and in other areas of an internal combustion engine has substantial relevance to combustion efficiency, engine performance, emissions control, and fuel/lubricant stability. Combustion by-products form films on combustion chamber walls that dramatically alter engine octane requirements. Other combustion by-products enter the lubricant system and undergo surface catalyzed polymerization and oxidation reactions resulting in films on pistons that contribute to wear. The same by-products dramatically enhance the degradation of the lubricant itself in complex processes known to involve surface reactions.

Progress on issues discussed in each of the previous subsections will unquestionably improve understanding in each of these technology areas. Attention should be given to the design of synchrotron-based experiments that can be carried out under conditions that better mimic the system of interest. Fluorescence yield NEXAFS (FYNES) is attractive in that it may be carried out under pressure. While it may not be possible to analyze the resulting spectra from first principles, a database of "fingerprint" spectra to assist in the analysis is feasible. IRAS is similarly amenable to the presence of an atmosphere, and could provide extremely useful characterization of the evolution of overlayer structures associated with films, corrosion, and wear. In ex-situ experiments, surface analysis using new microscopy methods and EXAFS could enhance our knowledge of these interface environments.

Another surface of large technological significance is the **solid/liquid interface, especially the electrified solid/liquid interface** between a solid and an ionically conducting liquid. These interfaces play a role in a variety of phenomena such as aqueous corrosion and electrochemical energy conversion and storage, i.e. batteries and fuel cells. Synchrotron radiation-based experiments to study this interface are still in the exploratory stage, but are rapidly increasing in number. In principle, the solid/liquid interface is more difficult to study than the gas/solid interface, but less difficult than the solid/solid interface, since the liquid phase is a less absorbing medium at XUV and x-ray wavelengths. Examples of synchrotron radiation experiments underway include conventional EXAFS of electrode materials and electrolytes, grazing incidence x-ray scattering of electrode surfaces, and NEXAFS of electrode surfaces under conditions of total reflection. **There are many theoretical challenges associated with the**

use of synchrotron radiation to study the electrified interface. One interesting aspect of NEXAFS of surfaces in electrolytes that has a unique theoretical challenge is the resonant capture by ions in the double-layer of low energy photoelectrons emitted by core excitation of atoms in the electrode surface. Such photoemission into solution complicates the interpretation of NEXAFS spectra for electrode surfaces, and theoretical treatment of these events will be necessary to fully exploit this technique. In fact, theoretical treatment of photoemission into a medium of solvated ions may suggest interesting new experimental techniques which could be exploited by a synchrotron light source, with its broad range of tunable high-resolution light.

5. Executive Summary

A number of primary directions for future research emerge from this workshop. These are also the areas which we strongly recommend for theoretical emphasis: they promise the greatest opportunities for fruitful interaction with experimental work conducted at synchrotron radiation facilities, in particular the ALS. After listing these major directions, which could form a set of large research programs, we shall identify more specific subjects needing close attention.

This workshop identifies the following *major topics for theoretical emphasis over the next decade*:

- **solid/solid interfaces: study of growth, especially for very heterogeneous interfaces (e.g. ionic/covalent), epitaxy, cross-diffusion and segregation; sandwiched impurities and monolayers at interfaces;**
- **solid/liquid interfaces: development of atomistic principles of electrochemistry and techniques for their investigation;**
- **structure and properties of stepped, kinked and defected surfaces, including disorder;**
- **less studied compound surfaces to be investigated in connection with catalytic, tribological and other applications: oxides, sulfides, nitrides, carbides;**
- **surface flexibility: relaxation, restructuring and elasticity, including the effect of adsorbates and interfaces;**
- **molecular adsorption structure and dynamics, for catalysis and tribology: studies as function of substrate material, crystallographic face, adsorbate, coadsorbate (promoters, poisons, additives);**
- **molecular surface and interface structures: from ice and polymer surfaces, thin films and interfaces to biological structures;**
- **magnetism of surfaces, thin films and interfaces;**
- **surface and interface excitations.**

In the following we shall list in more detail materials and subjects of research that are deemed to deserve additional emphasis. Most of these expand or refine the above broad areas of primary focus. First, a number of *materials* need to be given additional attention, due to their technological relevance and their underrepresentation in past studies:

- metal/metal and oxide/metal interfaces;
- alloys;
- insulators (SiO_2, Al_2O_3, $BaTiO_3$, etc.);
- high-T_C materials, zeolites and other polyatomic solids, including sulfides, oxides, nitrides, carbides;
- glasses;
- magnetic surfaces, thin films and interfaces;
- intercalated internal surfaces (as in graphite, MoS_2 and clays);
- molecular crystals (ice) and polymer surfaces;
- biologically important surfaces.

Next, *structural determinations* are considered highly desirable in the following areas:

- new or poorly studied surfaces and interfaces, such as:
  - epitaxial interface structures;
  - complex reconstructions and adsorbates, with large unit cells and many unknown structural parameters, possibly with disorder or incommensurate lattices;
  - stepped and kinked surfaces, and other defected surfaces, both clean and adsorbate-covered;
  - families of molecular adsorbates, ordered or disordered, pure or coadsorbed with promoters and poisons;
  - other materials and interfaces, in particular diamond, Ge and compounds (like oxides, carbides, nitrides and sulfides);
- surface segregation profiles;
- nature and relevance of adsorbate-induced restructuring (ranging from small relaxations to new compound formation).

Areas can be identified in which the *theory of electronic structures* needs to be directed or reinforced:

- need for more efficient computational total-energy techniques for more complex systems: surfaces, interfaces, disordered alloys, reconstruction, defects, steps, molecular adsorption;

- need for theoretical accuracies comparable with improved experimental accuracies at synchrotron radiation facilities;
- development of better embedding techniques, e.g. for coupling adsorbates or interfaces to a bulk;
- exploration of total-energy calculations with disorder (CPA and beyond);
- need for techniques to deal with impurities and sandwiched matter at interfaces: issues of cross-diffusion, interface sharpness, non-equilibrium, high temperature, different time scales, dynamics;
- extension of the theory of superlattices: need for theory to predict interesting superlattices (to understand and solve interface formation, which is difficult for strongly different materials, especially the ionic/covalent combination; issues of variable stoichiometry, dielectric discontinuity, strain/defects);
- need for techniques to deal with cases where many-body effects dominate;
- need to describe properties of new magnetic surfaces, thin films and interfaces, as well as layered structures;
- development of theoretical treatments of excited states, for fundamental understanding of many important processes and of the relationship to the many experimental data which involve excited states, following the example of the self-energy quasi-particle approach.

In the field of *surface reactions and dynamics*, we identify the following items for theoretical attention:

- study of the surfaces of oxides, other compounds and bimetallics as catalysts;
- understanding of the atomic-scale role of metal/oxide interfaces: strong metal-support interaction (SMSI effect);
- exploration of the nature of strong adsorbate-adsorbate interactions implicated in reactions;
- study of individual reaction steps (adsorption, desorption, thermal activation, bond breaking, bond formation, diffusion);
- study of complex adsorbates;
- identification of active reaction sites (such as defects);
- development of methods to describe networks of multiple pathways with closely competing energetics;
- comprehensive modeling of large classes of reactions, with at least qualitative predictive power;

- elucidation of the mechanisms of oscillatory and periodic reactions;
- study of long-range phenomena (promoters, poisons, adsorbate-induced reconstruction);
- dealing with the complexity of real catalyst materials;
- modeling the dynamics of large systems (with thousands of atoms): phase transitions, alloy segregation, diffusion, crystal growth, epitaxy;
- modeling the dynamics of non-rigid surfaces (electronically non-adiabatic) and ability to treat molecular dynamics and electronic structure self-consistently;
- description of dynamics at short time scales;
- fundamental studies of tribology (adhesion, elastic/plastic deformation, friction, lubrication, wear, fracture, hard coatings, passivation);
- development of a microscopic dynamical theory for interacting adsorbates at high concentrations;
- atomistic theory of solid/liquid interfaces and phenomena.

Regarding *experimental techniques* and their theoretical description, the following topics require further study:

- development of electron holography (which promises better resolution than electron microscopy), exploration of its capabilities, improvement of its resolution, interpretation with multiple scattering rather than plane-wave states (due to strong forward scattering);
- development of forward focusing of electrons and other diffraction effects of emitted electrons, with extension of their scope and accuracy;
- further implementation and development of direct methods in LEED and other techniques;
- introduction of faster multiple scattering calculations for LEED, ARPES, forward focusing, holography, etc.;
- automation of structure determination, especially with many unknown structural parameters;
- achievement of higher accuracy in diffraction theory (better than 0.01 Å possible?): better description of vibrations, inner potential, damping, beyond muffin-tin, relativistic corrections;
- resolution of remaining conflicts, such as between SEXAFS and other structure determination methods;
- need for theory of valence photoelectron diffraction;
- enabling structure determination of various types of defect structures.

Acknowledgements

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Appendix. Workshop Program

Program for
ALS Workshop on Challenges for Interface Theory

August 20-24, 1990

Lawrence Berkeley Laboratory
Building 50 Auditorium

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MONDAY, AUGUST 20, 1990
     ---------------------------------------------------------------
     8:40-8:50am   Opening: M.A. Van Hove (Lawrence Berkeley Lab.)

     8:50-9:00am   Welcome: A. Robinson (Advanced Light Source,
                                         Lawrence Berkeley Laboratory)

     ---------------------------------------------------------------
     INTERFACES I, L.M. Falicov, presiding

     9:00-9:35am   M. Weinert (Brookhaven National Laboratory):
                         Theory of Metal/Metal Interfaces and
                         Surface Adsorption

     9:45-10:20am  P. Pianetta (Stanford and SSRL):
                         Solid/Solid Interfaces and Microscopies

     ---------------------------------------------------------------
     INTERFACES II, M.A. Olmstead, presiding

     11:00-11:35am D.J. Chadi (Xerox PARC):
                         Theory of Solid/Semiconductor Interfaces

     11:45-12:20am A. Gonis (Lawrence Livermore National Laboratory):
                         Electronic Structure Theory
                         at Solid/Solid Interfaces
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EXPERIMENTAL METHODS AND FACILITIES, P.N. Ross, presiding

2:00-2:35pm Y. Petroff (LURE, Universite Paris-Sud):
Prospects in Electronic Structure
Measurements at Surfaces

2:45-3:05pm A. Robinson (Lawrence Berkeley Laboratory):
Opportunities at the Advanced Light Source

ELECTRONIC STRUCTURE, D. de Fontaine, presiding

3:45-4:20pm F. Himpsel (IBM Yorktown Heights):
Electronic Structure at
Semiconductor Interfaces

4:30-4:50pm S.G. Louie (LBL and University of California):
Theory of Electron Excitations
on Semiconductor Surfaces

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TUESDAY, August 21, 1990

TECHNIQUES, M.A. Van Hove, presiding

9.00-9:35am J.B. Pendry (Imperial College):
Electron Scattering Theories at Interfaces

9:45-10:20am C.S. Fadley (University of Hawaii):
Surface Structures from Photoelectron and
Auger Electron Emission: Recent Developments
and Theoretical Issues

11.00-11:35am S.Y. Tong (University of Wisconsin):
Theory of Electronic Emission from Surfaces
and Interfaces

11:45-12:05am M.A. Olmstead (LBL and University of California):
Synchrotron Radiation and Interfaces

SURFACE CHEMISTRY AND DYNAMICS, A. Chakraborty, presiding

2:00-2:35pm T. Upton (Exxon Res. & Eng. Co.):
Theory of Surface Chemistry

2:45-3:05pm G.A. Somorjai (LBL and University of California):
Challenges in Surface Chemistry

and Tribology

3:15-3:35pm K.B. Whaley (University of California):
Theory of Surface Dynamics

THEORY AND APPLICATIONS, S.G. Louie, presiding

4:15-4:35pm L.M. Falicov (LBL and University of California):
Electron Spectroscopy of Highly
Correlated Metals

4:45-5:05pm M.A. Van Hove (Lawrence Berkeley Laboratory):
Perspectives and Discussion

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WEDNESDAY, AUGUST 22 - FRIDAY, AUGUST 24

Closed workshop meetings, Building 2

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