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INTRODUCTION

In studies of the chemistry of surfaces we would like to rely on our knowledge of four fundamental properties.[1] These are: 1) The structure of the surface. Direct determination of the atomic surface structure is just as important as determination of the structure of solids by x-ray diffraction. Macroscopic irregularities such as steps and dislocations at surfaces influence many of the surface chemical properties. 2) The thermodynamic properties of surfaces. Thermodynamic studies would allow us to determine which crystal faces of solids would be likely to form under a variety of experimental conditions. From surface thermodynamic properties we should be able to predict the surface composition of multi-component systems (alloys, solutions) and predict changes of surface free energy upon adsorption, adhesion, or lubrication. 3) The dynamics of surface atoms. We should gain information about the energy and displacement of the surface atoms as they vibrate about their equilibrium lattice position since these are important parameters in the energy transfer during surface chemical reactions. Surface diffusion studies reveal the mechanism of which atomic transport occurs along the surface. The understanding of surface diffusion kinetics is also essential in uncovering the mechanism of many surface chemical reactions. 4) The electrical properties of surfaces. These studies uncover the nature of charge transport processes at the surface (conduction by mobile electrons or ions) which, in turn, should permit us to assess the possible role of mobile charges in chemical surface processes. The emission properties of solid surfaces (electron-emission, ion-emission) yield information about the electronic structure at the surface, about the composition of the surface, and of changes of charge distribution (space charge, charge transfer) in a particular chemical interaction with adsorbing species.

We wish to know these fundamental properties not only for the clean surface but also for the molecules in the adsorbed layer. All of these

properties are to be considered and taken into account in studies of more complex surface chemical reactions that so frequently occur in biochemical systems and in the chemical technologies.

Our understanding of these physical-chemical properties of surfaces until recent times has been poor when compared to our knowledge of these properties for atoms or molecules in the gas phase or in the solid state. The reason for our lack of information about surface properties becomes clear when we compare the density of surface atoms with the density of atoms in the bulk of the solid. A typical solid, like silver, has a bulk density of about 5.9×10^{22} atoms/cm^3. The surface density of atoms can be estimated to be approximately the 2/3 power of the volume density that is equal to 1.5×10^{15} atoms/cm^2. Thus in any experiment that is aimed at studying the surface one attempts to investigate the properties of $\approx 10^{15}$ atoms/cm^2 in the background of a much larger concentration of bulk atoms. Clearly, we need experimental techniques that are sensitive only to the topmost monolayer at the surface. In the past, the development of surface chemistry was hampered by the scarcity of experimental tools that provide information about the surface layer only, without containing a great deal of bulk information. Surface chemists, therefore, were forced to prepare and carry out measurements on samples of high surface/volume ratio, i.e., small particles. Since dispersed particles of small size are very important in many fields of applied surface science (heterogeneous catalysis, photography, colloid science) most fundamental physical-chemical properties of surfaces were naturally studied in this medium. Many ingenious experiments were carried out to determine the particle sizes accurately, to measure the amount of gas adsorbed on the surface of the particles, and to monitor the rates of chemical reactions that take place. Although studies of the various properties of the clean particle surfaces were difficult to carry out, a great deal of knowledge of the properties of adsorbed gases and liquids has been accumulated this way. of the thermodynamic properties (heats of adsorption, adsorption isotherms) of the adsorbed layer on dispersed particles have been determined, and even the area occupied by some of the adsorbed molecules has been measured.

In spite of the very large efforts of generations of ingenious experimentalists in surface science, there were serious limitations to the investigations of some of the fundamental properties of clean and gas-covered surfaces through studies of such dispersed systems of small particles. The atomic structure of the surface was unknown. Often, the surface information that is to be extracted from changes of experimental parameters was only a small fraction of the total change and was of the magnitude of the experimental uncertainty. For example, surface heat capacity measurements using small particles have been attempted by many, but succeeded only rarely. Due to the sometimes overwhelming difficulties of surface studies surface science became technique-oriented; certain measurements were applicable to studies of the surfaces of a small group of materials under well defined but limited experimental conditions. Such methods of study, although they have led to striking advances in certain limited areas of surface science (for example, studies of monomolecular layers of organic solids on liquid surfaces) have not much helped the development of surface chemistry as a whole as a field of science where fundamental physical-chemical properties are to be established and to be used as building blocks to understand the properties of complex surface systems. Surface chemistry (not unlike many other fields of chemistry) like a tree with many branches but without a trunk. Regretfully, in the absense of fundamental physical-chemical information about surfaces, surface chemistry teaching has been reduced in most university chemistry departments to a few lectures as a part of a physical chemistry course, and research on the fundamental properties of surfaces is not being actively pursued in most laboratories.

From the middle 1950's, however, there have been several technological developments which focused renewed attention to surfaces and to studies of their physical-chemical properties. Semiconductor devices with large surface to volume ratios necessitated a better understanding of the structural and electrical properties of clean surfaces. Single crystals in ultra high purity (impurity concentration in the parts per million ranges) became available in ever-increasing numbers and found technological use. Due to our efforts of space exploration, modern vacuum technology has developed to unprecedented levels such that the

attainment of ultra high vacuum (less than 10^{-8} torr) became available at a moderate cost and reasonable experimental times (hours). The ambient gas flux striking a surface at 10^{-6} torr is large enough ($\approx 10^{15}$ molecules/cm^2 sec) to cover a surface of typical atomic density if every molecule incident on the surface sticks. At 10^{-8} torr there is at least 100 seconds available before a monolayer adsorbs on the surface. Thus the attainment of ultra high vacuum made the study of clean surfaces possible for the necessary experimental times. It became clear that studies of the fundamental properties of surfaces should be carried out, whenever possible, on initially clean and preferably single-crystal surfaces. Experimental evidence began to accumulate, indicating that the crystal orientation is an important variable in the determination of the reactivity of surfaces. Today experiments can be carried out on one face of a clean crystal in ultra high vacuum with relative ease. Many new experimental techniques became available in recent years that can be applied, broadly, to the studies of most surfaces (for example, low energy electron diffraction, auger emission spectroscopy, ellipsometry, etc.). As a consequence, the physical-chemical properties of surfaces are being uncovered at an unprecedented rate.

The structure, the thermodynamics, the dynamics and the electrical properties of clean surface and of the adsorbed layer are presently the subjects of detailed investigations by surface chemists. We shall review our understanding of each of the fundamental aspects of surface chemistry. We shall concentrate on present views and understanding of these properties. All of these surface properties should be considered and taken into account in studies of more complex surface chemical reactions.

THE STRUCTURE OF SURFACES

To the naked eye one face of a diamond crystal, bounded by high density atomic planes, looks flat and perfect. However, closer inspection of any freshly grown crystal surface by using an optical

microscope with fairly large magnification (100 X) reveals large regions where the atoms are "dislocated" from their position in the surface plane to other parallel atomic planes separated from each other by ledges 10^2-10^5 Å high. For example, Figure (1) shows one face of a cadmium sulfide single crystal that exhibits a large concentration of these terraces. The growth of these terraces of parallel atomic planes is largely due to a small mismatch of atomic planes called dislocations in the bulk of the crystal.(2) These dislocations may propagate to the surface and growth of new atomic planes can begin at the emergence of these so-called "line defects."

There are several types of dislocations, depending on the way the mismatch has occurred in the bulk. Dislocation densities of the order of 10^4- 10^8 cm^{-2} are commonly observable on single-crystal surfaces that exhibit different chemical bonding properties. These concentrations may be compared with the surface concentration of atoms, which is on the order of $10^{15}cm^{-2}$. Thus each terrace that has developed out of a dislocation may contain roughly $(10^{15}/10^6) = 10^9$ atoms in a low-dislocation density single-crystal surface.

Using electron microscopy(3) to examine the structure of the seemingly ordered surface domains between dislocations at still larger magnification, we find that these atomic terraces are far from perfect. Figure (2) is a scanning electron microscope picture of a zinc crystal plane using a magnification of about 100,000. The surface is full of ledges--small stacks of terraces separated by steps 5-100 Å high. Thus the surface is heterogeneous even at this submicroscopic scale. Typically, in an area of $1\mu^2$($1\mu = 10^{-4}$ cm) one can distinguish several surface sites which differ by the number of neighbors surrounding them. These are shown schematically in Figure (3). A surface atom is surrounded by the largest number of neighbor atoms when it is located in an atomic plane; this number is reduced substantially for surface atoms along a ledge or a step.

Now let us consider the experimental techniques which are capable of viewing the surface on an atomic scale. Among these the most

frequently used are field ion microscopy[4] (FIM) and low energy electron diffraction (LEED).[5]

Field ion microscopy allows us to distinguish individual atoms in the different crystal planes. Under the influence of a large electric field ($\sim 10^9$ volts/cm) at a small crystal tip, helium atoms that are incident on the tip are ionized. The positive ions are then repelled from the surface radially and accelerated onto a fluorescent screen where a greatly magnified image of the crystal tip surface is displayed. The intensity on any part of the screen is proportional to the number of incident helium ions. Since the concentration of helium ions produced at each crystal surface depends upon the unique atomic and electron densities in the different surface planes, the various crystal surfaces of the tip end, even the various atomic positions, can be identified by studying the intensity contrast of the fluorescent screen.

Figure (4) depicts the image of a tungsten field ion tip. The uniform intensity in well-defined areas of the crystal surface is due to ion emission from given atomic planes that bound the tungsten tip. The fact that these crystal faces can be readily distinguished and identified indicates that they are ordered on an atomic scale, i.e., most of the surface atoms in any given crystal face are situated in ordered rows separated by well-defined interatomic distances. The field ion picture may also indicate the movement of a small number of surface atoms and identify the presence of point defects or vacancies in the surface. Surface atoms may move along one atomic plane and leave a vacancy--a vacant atomic position--behind. Thus, along with the atomic steps and ledges, single atoms and vacancies (point defects) are also distinguishable in atomically ordered crystal planes.

Another method which has revealed that the crystal surfaces are ordered on an atomic scale and which is most frequently used to study the structure of surfaces utilizes diffraction. In order to obtain diffraction from surfaces the incident wave has to satisfy the condition $\lambda \leq d$, where λ is the wave-length of the incident beam and d is the interatomic distance in the surface. Also, the incident beam should not penetrate much below the surface plane but should back-diffract dominantly

from the surface so that the scattered beam reflects the properties of the surface atoms and not of atoms in the bulk. Low-energy electrons (5-500 eV) satisfy these conditions and low-energy electron diffraction is used almost exclusively at present to study the structure of crystal surfaces and the rearrangement of surface atoms which may take place as a function of temperature or exposure to gases.

The technique of a low-energy electron diffraction experiment is shown in Figure (5a), in which monochromatic electrons are shown back-scattering from one face of a single crystal. The elastically scattered fraction, i.e., those electrons that do not lose energy in the scattering process, contains the diffraction information. These electrons are allowed to impinge on a fluorescent screen on which the diffraction pattern is displayed.(5) A typical diffraction pattern from a clean (111) face of a platinum single crystal is shown in Figure (5b). The more that atoms are located in ordered rows in which they are separated from their neighbors by well-defined distances, the smaller are the diffraction spots and the higher their intensity. The presence of the small, high intensity diffraction spots clearly indicates that the surface is ordered on an atomic scale. Similar low-energy electron diffraction patterns have been obtained from solid single-crystal surfaces of many types.

Thus we can conclude that:

(a) The surface is heterogeneous on a microscopic and submicroscopic scale. One can distinguish atomic terraces separated by ledges--atomic steps of various heights. There are vacancies in surfaces and several atomic positions distinguishable by their different numbers of nearest neighbors.

(b) The surface appears to be well ordered on an atomic scale. Most of the surface atoms are located in ordered rows characterized by well-defined interatomic distances.

The Atomic Structure of Surfaces

Most of the surfaces studied by low-energy electron diffraction so far have been high density faces of monatomic or diatomic solids. Without exception, all of these faces exhibit ordered structures on an atomic scale. These ordered surfaces may be divided into two classes:[5] 1) those that have unit cells identical to the projection of the bulk unit cell to the surface and 2) those characterized by unit cells that are integral multiples of the unit cell dimensions in the bulk. The different crystal faces of tungsten, nickel and aluminum, for example, seem to belong to the first class. However, most semiconductors (Si, Ge, GaAs, InSb) and some of the metal surfaces studied so far (Pt, Au, Bi, Sb) belong to the second class. These surfaces exhibit diffraction patterns with extra diffraction features superimposed on the diffraction pattern of the substrate unit mesh (predicted by the bulk unit cell). For example the (111) face of silicon has unit cell dimensions that are identical to the bulk unit cell below 700°C. The corresponding diffraction pattern is shown in Figure (6a). At or above 700°C a new ordered surface structure forms as indicated by the appearance of new diffraction patterns (Figure 6b). The surface structure is now characterized by a unit cell that is seven times as large as the bulk unit cell along the (111) surface.

Surface structures of this type may be formed by a periodic displacement of surface atoms out of the surface plane. The surface would thus exhibit a periodic "buckling" giving rise to new, characteristic diffraction features. This mechanism may best be illustrated by considering the differences in the atomic environment of surface and bulk atoms.

Surface atoms are in an anisotropic environment as though they were surrounded by atoms on one side and by vacancies on the other. These atoms can "relax" by moving out of plane, perpendicular to the surface--a motion that is not allowed for the bulk atoms. Depending on the bonding properties of the solid, atoms may be displaced out of plane in a periodic manner. Calculations[6a,b] indicate that the formation of some of these

buckled surfaces can be energetically favored over the formation of flat surfaces in temperature ranges below the melting point of the solid. The appearance of any new surface periodicity will be reflected in the characteristics of the LEED diffraction pattern. It is likely that surface structural rearrangements in germanium, silicon, and other semiconductor surfaces take place by this mechanism.

It should be noted that the periodic out-of-plane surface relaxation should be very sensitive to the presence of impurities or to certain types of lattice defects emerging at the surface (dislocations and vacancies). These could cause the collapse of surface structures by changing the chemical environment about the surface atoms or, in some cases, could also catalyze their formation.

Some of the metal surfaces were also found to undergo atomic rearrangements. For example, the (100) surfaces of gold, platinum and iridium exhibit diffraction patterns that can be interpreted as indicating the presence of a hexagonal arrangement of scattering centers superimposed on the underlying square (100) substrate. The chemical properties of this surface structure [its sensitivity to chemisorbed gases] make it likely that the surface structure is again the result of periodic buckling of the surface plane. In this case, however, the surface relaxation resulted in the formation of a hexagonal surface structure, i.e., there is a change of rotational multiplicity (from 4-fold to 6-fold). For semiconductors the surface structure maintained the rotational multiplicity of the bulk unit cell except that the surface net became enlarged. It appears that these metal surfaces have undergone a phase transformation from a face centered cubic to a hexagonal close-packed surface structure while no corresponding transformation occurs in the bulk of the solid.

The crystal structure that a solid will take up has been shown[7a,b] to depend primarily on the number of unpaired s and p valence electrons per atom that are available for bonding. A theory based on this concept, when extended to include the contribution of unpaired d electrons to the binding, can explain and predict the structure and stability range of most alloys. Surface atoms, in addition to being

in an anisotropic environment, have fewer neighbors than atoms in the bulk of the solid. Therefore their electron density distribution may be different from that in the bulk, and they may have fewer or more valence electrons available for bonding than the bulk atoms. Thus they may undergo structural transformations in the surface plane with respect to their crystal structure in the bulk.

It should be noted again, just as in the case of surface relaxation, that impurity atoms with different numbers of unpaired valence electrons per atom may cause or accelerate surface phase transformations of this type on transition metal surfaces, or conversely, may inhibit it. For example, carbon (electron donor) stabilizes the f.c.c. surface structure on the platinum and gold (100) surfaces. On the other hand there appears to be evidence that oxygen adsorbed on these noble-metal surfaces may act as an electron acceptor and can stabilize the hexagonal surface structure.[5]

This mechanism of surface phase transformation would also predict the formation of surface alloys with a variety of structures and other interesting physical-chemical properties. These may be prepared by the deposition of other suitable metal atoms with different numbers of unpaired valence electrons.

There are several reports of ordered surface rearrangements induced by changes in the stoichiometry at the surface.[5] For example, the (0001) face of aluminum oxide (α-alumina), exhibits a surface structure characteristic of the bulk unit cell. Upon heating to 1200°C in vacuum, the surface structure changes; during this time there is also detectable oxygen evolution from the surface. When the oxygen deficient high temperature surface structure is heated in oxygen the original low temperature surface structure is restored. This reversible phase transformation could be induced at will upon introduction or removal of oxygen.

It appears that the high-temperature oxygen deficient surface structure has a composition that corresponds to Al_2O (or AlO). These oxides are stable species in the vapor phase but are not thermodynamically stable in the solid state.

If the reduced oxides of aluminum, Al_2O or AlO, are stable in the α-alumina surface at elevated temperatures, it is likely that the other thermodynamically unstable oxides might also be stabilized in the surface environment. Vanadium pentoxide, V_2O_5 shows similar structural changes upon variation of the surface chemical composition.(5)

THERMODYNAMICS OF SURFACES

The thermodynamic properties associated with surfaces are, in general, defined separately from the bulk thermodynamic properties.(8) Consider a large homogeneous crystalline body that contains N atoms and is surrounded by plane surfaces. The energy of the solid per atom is denoted by E^o. The specific surface energy, E^s (energy per unit area) is defined by the relation

$$E = NE^o + \mathcal{A}E^s \qquad (1)$$

where E is the total energy of the body and $\mathcal{A}$ is the surface area. Thus E^s is the excess of the total energy E that the solid has over the value NE^o, which is the value it would have if the surface were in the same thermodynamic state as the homogeneous interior. The other surface thermodynamic variables (surface entropy, surface free energy, etc.) are defined similarly.

In order to create a surface we have to do work on the system that involves breaking bonds and removing neighboring atoms. Under conditions of equilibrium at constant temperature and constant pressure the reversible surface work δW^s required to increase the surface area $\mathcal{A}$ by an amount $d\mathcal{A}$, of a one component system, is given by

$$\delta W^s_{T,P} = \gamma \, d\mathcal{A} \qquad (2)$$

Equation (2) can be compared with the reversible work to increase the volume of a one component system at constant pressure, PdV. Here

γ is the two dimensional analogue of the pressure and is called the "surface tension" while the volume change is substituted for by the change in surface area. We may consider γ as a pressure along the surface plane that opposes the creation of more surface. The pressure, P, is force per unit area (dyne/cm^2); therefore the "surface pressure," γ, is given by force per unit length (dyne/cm). (The customary units of surface tension, dyne/cm or erg/cm^2 are dimensionally identical.) In the absence of any irreversible process the reversible work, $\delta W^s_{T,P}$ is equal to the change in the total free energy of the surface. The total surface free energy is thus equal to the specific free energy times the surface area $\delta W^s_{T,P} = d(G^s A)$.

Creation of a stable interface always has a positive free energy of formation. This reluctance of the solid or liquid to form a surface defines many of the interfacial properties of the condensed phases. For example, liquids tend to minimize their surface area by assuming a spherical shape. Solids, when they are near equilibrium with their own liquid or vapor, will form surfaces of lowest free energy at the expense of other surfaces of higher free energy. Crystal faces, which exhibit the closest packing of atoms, tend to be surfaces of lowest free energy of formation and hence the most stable.

The surface tension may be equal to the specific surface free energy for a one-component system. These terms are frequently used interchangeably in the literature. Typical surface tension values are Cu Cu(liq) = 1300 ergs/cm^2, NaCl(s) = 227 ergs/cm^2, benzene(liq) = 28.8 ergs/cm^2, and H_2O(liq) = 72.7 ergs/cm^2. There are many different experimental techniques to measure surface tensions of liquids and solids.[10]

The specific surface entropy, S^s, may be determined from the temperature dependence of the surface tension. The surface tension of most liquids decreases with increasing temperature. This indicates that the work necessary to create more surface decreases with increasing temperature. Semi-empirical equations for predicting the temperature dependence of the surface tension have been proposed.

There may be systems where the surface becomes more ordered with increasing temperature; such surface ordering would be indicated by the γ-vs-T curves. Positive slopes of the γ-vs-T curves have been reported from studies of the temperature dependence of the surface tension of copper and zinc.[1] On the other hand, the surface may become disordered faster than the corresponding bulk phase. Thus determination of γ as a function of temperature provides a great deal of information about ordering at the surface.

The temperature derivative of the specific surface entropy is the specific surface heat capacity

$$C_P^s = -T\left(\frac{\partial S^s}{\partial T}\right)_P = -T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)_P \qquad (3)$$

Although many of the γ-vs-T curves show marked curvature, $(\partial S^s/\partial T \neq 0)$, instead of a straight line (i.e., $\partial S^s/\partial T = 0$), the data is not accurate enough to permit computation of reliable surface heat capacity values.

Surface Tension of Multicomponent Systems

The total free energy change of a multicomponent system can be expressed, with the inclusion of the surface term,[8] as

$$dG = -SdT + VdP + \gamma d\mathcal{A} + \sum_i \mu_i dn_i \qquad (4)$$

Consider now the free energy change for the process in which the surface area is increaeed by $d\mathcal{A}$ by transferring dn_i moles from the bulk to the surface at constant temperature and pressure. We have

$$dG_{T,P} = \gamma d\mathcal{A} - \sum_i \mu_i dn_i \qquad (5)$$

where the negative sign indicates the decrease of the bulk concentration of the ith component. This e tion shows that the surface tension, γ, cannot be identified with the total surface free energy per unit area for a multicomponent system. For single-component systems or for systems in which any change in the surface area does not cause changes in the surface composition, $dG_{T,P,n} = \gamma d\mathcal{A}$.

The change in surface tension as a function of temperature and surface composition is given by

$$d\gamma = - S^s dT - \sum_i C_i^s \, d\mu_i \qquad (6)$$

where C_i^s is the surface concentration of the ith component in units of moles/cm^2.[6] This equation was first derived by Gibbs[9] and it is commonly called the Gibbs equation. Just like the free-energy relations for bulk phases it predicts the changes in surface properties that should occur as a function of the different experimental variables. Detailed discussion of the dependence of $d\gamma$ on the surface composition in a multicomponent system is outside the scope of this paper. Excellent treatments of the surface thermodynamics of multicomponent systems of many types (liquid-gas, liquid-solid, liquid-liquid) are available in the literature[4]. One of the important pieces of information obtainable from the Gibbs equation is the variation of the surface tension γ with changes of the surface concentration of the second component.

Surface Energies of Various Solids and Different Crystal Faces

There have been several calculations carried out to estimate the specific surface energies and surface tensions for different crystal faces of ionic, metal, and noble gas crystals.[11] In these computations a suitable potential function is used that gives the potential energy of interaction between pairs of particles as a function of the distance of separation only. Then the total energy for the surface layer is obtained as the sum of the interactions of the pairs.

The computations in general are carried out in two parts. First a surface is "produced" by "breaking bonds," that is, by removing atoms

opposite the surface atoms. During this process the atoms in the newly created surface are held rigidly in equilibrium positions, which they would have occupied in the bulk of the solid. Then the surface atoms are allowed to "relax" into new equilibrium positions by displacement perpendicular to the surface plane. This relaxation process always decreases the total specific surface energy. The specific surface energy may be written as

$$E^S = E^S(0) + \Delta E^S \qquad (7)$$

where $E^S(0)$ is the specific surface energy of the rigid lattice and ΔE^S is the relaxation energy. These two terms have opposing signs.

The results of these computations are very sensitive to the properties of the potential function used and to the atom or ion sizes assumed. Because of these difficulties the computed values are only significant for indicating the order of magnitude of the specific surface energies and relaxation energies. The magnitudes of the specific surface energies for the different solids roughly parallels their heats of atomization; the weakly bonded rare gas crystals have low specific surface energies (20-60 ergs/cm^2). Also, their specific relaxation energies are only a small fraction (< 1%) of the total surface energy. For singly charged ionic crystals the specific surface energies are almost an order of magnitude higher (100-300 ergs/cm^2) than for rare-gas crystal surfaces.[11] The relaxation energies are very high, 20-50% of $E^S(0)$, because of the polarization effects. For metals the specific surface energies are even high (400-1000 ergs/cm^2), but the relaxation energies are small -- no more than 2-6% of $E^S(0)$.

Another important result of these calculations is that in order to obtain minimum specific surface energies the surface layer had to be displaced outward, away from the second atomic plane by 2-8% of the interplanar distance. Most of the computations predict lattice expansion at the surface. For ionic crystals the positive and negative ions in the surface may be displaced in opposite directions or in the same direction,

depending on the relative ion sizes. These calculations also indicate that surface distortions are restricted to the proximity of the surface layer.

In equilibrium the crystal will take up a shape that corresponds to a minimum value of the total surface free energy. Thus a stable crystal will primarily be bounded by crystal faces with the lowest surface tension since $G^s_{total} = G^s \not{A} = \gamma \not{A}$. In order to have the equilibrium shape, the integral $\int \gamma d\not{A}$ over all surfaces of the crystal must be a minimum. If the specific surface free energies or surface tensions of the various crystal faces were known, we could easily construct the stable crystal shape. Crystals rarely take up this equilibrium shape because they are, in general, prepared by nonequilibrium processes. However, if a small crystal is heated close to its melting point in equilibrium with its vapor, where atoms will have sufficient mobility to rearrange, the crystal may approach the equilibrium form.

The relative surface tension of different crystal faces may be determined experimentally.[11] Typical surface tension ratios are: $[\gamma(111)/\gamma(100)]_{Cu} = 0.95$; $[\gamma(100)/\gamma(110)]_{Cu} = 0.91$.

Thermodynamic Properties of Curved Surfaces

Solids and liquids will always tend to minimize their surface area in order to decrease the excess surface free energy.[1] For liquids, therefore, the equilibrium surface becomes curved where the radius of curvature will depend on the pressure difference on the two sides of the interface and on the surface tension.[9]

In Figure (7) we have an equilibrium curved surface (a bubble, in this case) with internal and external pressures p_{in} and p_{ext}, respectively, and with a surface tension, γ. In equilibrium the radius of curvature, r, is related to these quantities as

$$\left(p_{in} - p_{ext}\right) = \frac{2\gamma}{r} \qquad (8)$$

This equation is quite significant in explaining the properties of liquid surfaces and of bubbles. First of all, it indicates that in equilibrium a pressure difference can be maintained across a curved surface. The

pressure inside the liquid drop or gas bubble is higher than the external pressure, because of the surface tension. The smaller the droplet or larger the surface tension, the larger the pressure difference that can be maintained. For a flat surface $r = \infty$, and the pressure difference normal to the interface vanishes.

Let us now consider how the vapor pressure of a droplet depends on its radius of curvature r. We obtain

$$\ln \frac{P}{P_o} = \frac{2\gamma V_m}{RT\, r} \qquad (9)$$

which is the well-known Kelvin equation for describing the dependence of the vapor pressure of any spherical particle on its size.[1] P_o is the vapor pressure over a flat surface [$(1/r = 0]$, and V_m is the molar volume. We can see that according to Equation (9), small particles have higher vapor pressures than larger ones. Similarly very small particles of solids have greater solubility than large particles. If we have a distribution of particles of different sizes we will find that the larger particles will grow at the expense of the smaller ones, as predicted by Equation (9).

It should be noted that such differences in vapor pressure or solubility that depend on particle size (radius of curvature) can only be observed for particles smaller than $r \leq 100$ Å. If we assume representative values for a water droplet ($\gamma = 72.7$ erg/cm^2, $\bar{V}_m = 18$ cm^3/mole), P/P_o approaches unity rapidly above this radius.

The shape of the curved surface, in turn, allows one to determine the surface tension of the liquid when it is in equilibrium with its own vapor or to determine the "interfacial tension" if the droplet is in contact with a different substance (gas, liquid, or solid) instead of its own equilibrium vapor. The interfacial tension is determined by measuring the "contact angle" at the liquid-solid and solid-vapor interfaces. The contact angle is defined in Figure (8), which shows a typical liquid-solid interface. Common experience tells us that the smaller the contact angle between the liquid and the solid the more evenly is the liquid

spread over the solid surface, until at $\theta \approx 0$ complete "wetting" of the solid surface takes place. If the contact angle is large ($\theta \to 90°$) the liquid does not readily wet the solid surface. For $\theta > 90°$ the liquid tends to form sphere-shaped droplets on the solid surface that may easily run off, i.e., the liquid does not wet the solid surface at all.

Remembering that the interfacial tension always exerts a pressure tangentially along the surface,[12] the surface free-energy balance between the surface forces acting in opposite directions is given by

$$\gamma_{lg} \cos \theta + \gamma_{sl} = \gamma_{sg} \quad \text{or} \quad \cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \qquad (10)$$

Here γ_{lg} is the interfacial tension at the liquid-gas interface, γ_{sg} and γ_{sl} are the interfacial tensions between the solid-gas and solid-liquid interfaces, respectively. Thus in equilibrium at the solid-liquid-gas interface, from the knowledge of γ_{lg} and the contact angle, we can determine the <u>difference</u> $\gamma_{sg} - \gamma_{sl}$ but not their absolute values.

There are extreme cases when Equation (10) does not define the equilibtium position of the line of contact. Therefore it is more convenient to consider the wetting coefficient

$$k = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \qquad (11)$$

in describing the wetting ability of a liquid. If $k \geq +1$ the solid is completely wetted by the liquid. For k values between ± 1 the wetting is described by Equation (10), and for $k \leq -1$ the solid is not wetted at all. Since the wetting ability of the liquid at the solid surface is so important in practical problems of adhesion or lubrication, there is a great deal of work being carried out to determine the interfacial tensions for different combinations of interfaces.[12] It is, for example, useful in these studies to determine the energy necessary to separate the solid-liquid interface. Harkins and his co-workers have defined the work of adhesion by defining the second state in which the solid and liquid phases are separated to be in a vacuum.[13] Thus the work of adhesion is defined

as

$$W_A^s = \gamma_{l,o} + \gamma_{s,o} - \gamma_{sl} \qquad (12)$$

where $\gamma_{l,o}$ and $\gamma_{s,o}$ are the surface tensions of the liquid and the solid, respectively, in vacuum.

In measurements of the contact angle the surface roughness plays an important role. Surface heterogeneities may modify the contact angle markedly with respect to that on a smooth solid surface.

In general, solids and liquids that have large surface tensions form strong adhesive bonds, i.e., have large negative works of adhesion. The work of adhesion ranges from -40 ergs/cm^2 for solid-liquid pairs that have low surface tension to as high as -140 erg/cm^2 or greater for solid-liquid interfaces that have high surface tensions before joining them together.[12]

Nucleation

Since the free energy energy of formation of a surface is always positive, a particle that consists only of surfaces, i.e., platelets or droplets of atomic dimensions, would be thermodynamically unstable. This is also apparent from the Kelvin equation [Equation (9)], which states that a particle that falls below a certain size will have an increased vapor pressure and therefore evaporate. There must be a stabilizing influence, however, that allows small particles of atomic dimensions to form and grow -- a common occurrence in nature. This is given by the free energy of formation of the bulk condensed phase. The total free energy of a growing particle is

$$\Delta G_{(total)} = -nRT\ln(P/P_{eq}) + 4\pi r^2\gamma \qquad (13)$$

In order to see the dependence of ΔG on the dimensions of the condensed particle let us substitute for n, the number of moles of condensed

vapor, $n = \left(\frac{4}{3}\pi r^3\right)/V_m$, where $V_m = M/\rho$ is the molar volume of the condensed phase, M is its atomic weight, and ρ is the density. We have

$$\Delta G_{(\text{total})} = -\left(\frac{4}{3}\pi r^3/V_m\right) RT \ln(P/P_{eq}) + 4\pi r^2\gamma \qquad (14)$$

Initially, when the condensed particle is very small, the surface free-energy term must be the larger of the two terms on the right-hand side of Equation (14), and ΔG increases with r. In this range of sizes the particles are unstable. Above a critical size, however, the volumetric term becomes larger and dominates, since it increases as $\sim r^3$ but the surface free-energy term increases only as $\sim r^2$. Hence the particle of that size or larger grows spontaneously (for $P > P_{eq}$). When ΔG is at a maximum, that is, $\partial\Delta G_{(\text{total})}/\partial r = 0$, the particle reaches the critical size it must have for spontaneous growth to begin:

$$r(\text{critical}) = \frac{2\gamma V_m}{RT \ln(P/P_{eq})} \qquad (15)$$

r(critical) is about 6 - 10 Å for most materials, which indicates that the droplet of critical size contains between 50-100 atoms or molecules.

A condensed particle must be larger than a certain critical size for spontaneous growth to occur at pressures $P > P_{eq}$. "Homogeneous nucleation" of the condensed phase by simultaneous clustering of many vapor atoms to reach this critical size, however, is very improbable. This is the reason that "supersaturated vapor" can exist; i.e., ambient conditions in which vapor pressures are larger than the equilibrium vapor pressure $(P > P_{eq})$ of a condensible substance can be established without the formation of the condensed phase. Precipitation in the absence of nuclei is very difficult, and large pressures much higher than the equilibrium vapor pressure $(P \gg P_{eq})$ must be established before condensation could occur within reasonable experimental times. Supersaturated vapor or undercooled liquid (cooled many degrees below its freezing point) are common occurrences in nature and in the laboratory.

Because of the difficulty of homogeneous nucleation, growth of condensed phases generally occur on solid surfaces already present such as the walls of the reaction cell or dust particles present in the atmosphere or in interstellar space. The introduction of solid crystallites to induce the formation and growth of the condensed phase is frequently called "seeding" or "heterogeneous nucleation." It is used to facilitate the growth of crystals or the condensation of water droplets from the atmosphere (rain-making).

DYNAMICS OF SURFACE ATOMS

Perhaps the most useful analogs in studying the vibration of surface atoms about their equilibrium position is the harmonic oscillator. The reason for the success of this simple model in exploring the dynamics of atomic motion in solids and in surfaces is that the displacement of the vibrating atoms is only a small fraction of their interatomic distance. Using the harmonic oscillator model, we can get near to describing the motion of surface atoms about their equilibrium position. The theory that describes the vibration of atoms in solids as harmonic oscillators which undergo quantized oscillations predicts well the total lattice energy, and lattice heat capacity of solids and their temperature dependence. The heat capacity of a monatomic solid at high temperatures is $C_v(T\to\infty) = 3\ R$ At low temperatures $C_v \simeq 234\ R\ (T/\theta_D)^3$ where θ_D is the Debye temperature of the solid. θ_D is related to the highest frequency of allowed atomic vibration.[9] One may also use the same model with confidence to evaluate the temperature dependence of the surface heat capacity due to vibrations of atoms in the surface. At high temperatures the total energy and the heat capacity for surfaces yield the same limiting value as that for three dimensional solids. At low temperatures the surface heat capacity C_v is proportional to T^2, as opposed to the T^3 dependence of the bulk lattice heat capacity. In most cases the solid samples that can be used in experiments are small particles of

variable surface-to-volume ratio or thin films many atomic layers thick. It would therefore be important to consider the heat capacity of such a sample and to see what contribution, if any, the surface makes to the total vibrational heat capacity. It appears that their film samples in the 10^{-5} - 10^{-4} cm thickness range should show a detectable contribution of surface heat capacity at low temperatures.

Mean Square Displacement of Surface Atoms

We may express the mean square displacement of harmonic oscillators[14]

$$\langle x^2 \rangle = \frac{3 N \hbar^2}{m k \Theta_D^2} T \qquad (16)$$

where m is the atomic weight, k and $\hbar$ are the Bolzman and Planck constants respectively. Thus the mean square displacement of atoms that vibrate as harmonic oscillators is linearly proportional to the temperature at high temperature.

It has been found by experiment that the intensity of diffracted low energy electrons or X-ray beams markedly depends on the temperature of the scattering solid.[15] The intensities of the diffracted beams decrease exponentially with increasing temperature. This is because of the fact that at any one instant many of the vibrating atoms are displaced from their equilibrium position. Thus the incident electron beam encounters a partially disordered lattice. The atoms that are displaced from their equilibrium position during the scattering process will scatter out of phase and a fraction of the elastically scattered electrons will be found in the background instead of in the diffraction spot. It can be shown that the intensity of a diffracted beam is given by[5]

$$I_{hk\ell} = |F_{hk\ell}|^2 \exp(-\alpha \langle x^2 \rangle) \qquad (17)$$

where α is a constant at a given wavelength and scattering angle. By substitution of Equation (16) into Equation (17) we see that the

diffracted beam intensity decreases exponentially with increasing temperature. By measuring as a function of temperature, the intensity of low-energy electrons diffracted from surface atoms, the mean square displacement of surface atoms can be obtained. The rms displacement of surface atoms in several cubic metals has been determined in this manner. The rms displacement of surface atoms, perpendicular to the surface plane, is 1.4 to 2 times as large as the bulk value. Similar large rms displacements were obtained for different crystal faces of the same solid in most cases.(5)

Since surface atoms have fewer neighbors than bulk atoms there is a reduction in the interatomic forces at the surface when compared with the bulk. We have seen many consequences of this already. For example, the mean square amplitude of atomic vibrations at the surface increased with a corresponding decrease in the vibrational frequencies. Another consequence of the creation of the surface is that certain modes of vibrations become localized, that is, these vibrations only propagate along the surface and their displacement dies out exponentially toward the interior of the crystal.

There have been few experimental studies aimed at determining the surface modes of lattice vibration. This important field of surface science still awaits innovations in experimental methods of measurement.

Surface Diffusion

We have so far discussed several phenomena associated with the vibration of surface atoms about their equilibrium positions. The thermal energy ($3RT \approx 1.8$ kcal/mole at 300° K) tied up in lattice vibrations is only a small fraction of the total energy necessary to break away an atom from its neighbors and to move it along the surface. This energy is on the order of 15-50 kcal/mole for many metal surfaces. Nonetheless, as the temperature of the surface is increased, more and more surface atoms may acquire enough activation energy to break bonds with their

neighbors and movel along the surface. Such surface diffusion plays an important role in many surface phenomena involving atomic transport; for example, crystal growth, vaporization, and adsorption. Surface diffusion is considered to be a multistep process in which atoms break away from their lattice position (for example, a kink site at a ledge) and migrate along the surface until they find their new equilibrium site.[16]

Let us assume that the only diffusing species are ad-atoms (adsorbed atoms) held by small binding energy on the surface with respect to surface atoms in other lattice positions. In order to move an ad-atom to a neighboring site, a certain amount of thermal energy is needed. Since the atom can only occupy equilibrium sites at the beginning and at the end of the jump on an ordered crystal surface, the atom in the region in between the ad-atom at this energy maximum and that at an equilibrium lattice site is designated ΔE_D. During its thermal vibration about the equilibrium site the atom strikes against this potential energy barrier ν_o times per second. The jump frequency to a neighboring site is given by $\nu_o \exp(-\Delta E_D/kT)$. Since the ad-atom can jump into η equivalent neighboring sites the total jump frequency f is given by

$$f = \eta \nu_o \exp(-\Delta E_D/kT) \qquad (18)$$

For a (111) face of a face centered cubic metal, $\eta = 6$; the vibrational frequency is on the order of 10^{12}sec^{-1}. Assuming that ΔE_D is 20 kcal/mole, at 300°K the atom makes one jump in every 50 seconds and at 1000°K on in 10^{-8} second. Thus we can readily see that the surface diffusion rate changes very rapidly with temperature.

Let us now consider that the ad-atom concentration in the surface is very small. Since we have assumed that surface diffusion can only occur via the motion of ad-atoms, these species have to be created before any appreciable diffusion can occur. The fraction of ad-atoms, C/C_o, in the surface is given by $C/C_o = \exp(-\Delta E_f/kT)$, where ΔE_f is the energy of formation of an ad-atom, C is the concentration of ad-atoms, and C_o is the total concentration of surface sites from which the ad-atom can

break away. Now, the total jump frequency is further reduced by another exponential factor:

$$f = \nu_o \eta \exp\left[-\frac{\Delta E_D + \Delta E_f}{kT}\right] \qquad (19)$$

So we see that any change in the mechanism of diffusion that affects the overall activation energy for the process can markedly change the jump frequency.

On a real surface many atoms diffuse simultaneously and their concentration could be in the range 10^{10} - 10^{13} atoms/cm^2. Therefore in diffusion experiments the measured diffusion distance after a given diffusion time is an average of the diffusion lengths of a large, statistical number of surface atoms. It is thus important to define the diffusion process in terms of macroscopic parameters.

The jump frequency [Equation (19)] characteristic of all of the diffusing atoms can be expressed as

$$f = \nu_o \exp\left(-\frac{\Delta F_D^*}{RT}\right) \qquad (20)$$

where ΔF_D^* is the increase in free energy in moving a mole of particles from their equilibrium energy state to their state at the top of the potential barrier. We define a diffusion coefficient, D, for two dimensional diffusion as $D = fd^2/4$. We can then rewrite Equation (20) as

$$D = \eta \frac{d^2 \nu_o}{4} \exp\left[\frac{\Delta S_D^* + \Delta S_f}{R}\right] \exp\left[-\frac{\Delta H_D^* + \Delta H_f}{RT}\right] \qquad (21)$$

By grouping the temperature-independent terms in Equation (21) into one constant, D_o, which is called the diffusion constant, and letting $Q = \Delta H_D^* + \Delta H_f$, where Q is often called the total activation energy for the overall diffusion process, we have

$$D = D_o \exp(-Q/RT) \qquad (22)$$

Surface diffusion studies on solid surfaces have been carried out by using several experimental techniques. Among these radioactive tracer diffusion and grain-boundary-grooving techniques appear to be those most frequently employed.[1]

The difficulty in most surface diffusion experiments is to determine the type of surface species moving along the surface. The overall diffusion rate can be determined with relative ease and the diffusion coefficient can be calculated. However, D obtained in this way does not give one direct information about the diffusing entities. The heterogeneous surface contains atoms in different lattice positions in which their binding energies are different. The surface diffusion measurements do not easily distinguish among the atoms to indicate which of the surface species contributes dominantly to the diffusion flux. The temperature dependence of D will give the overall activation energy of diffusion, Q. Its magnitude often enables one to distinguish between different overall mechanisms of surface transport. For example, if ad-atoms, already present on the surface in large concentrations, are the dominant contributors to the diffusion flux, the activation energy will be $Q = \Delta H_D$. If the ad-atom concentration is small and the diffusion process includes their formation and subsequent diffusion the activation energy will be greater and be given by $Q = (\Delta H_D^* + \Delta H_f)$.

It appears that the mechanism of surface self-diffusion of face centered cubic metals changes as a function of temperature. It has been suggested that, at low temperature, the motion of ad-atoms dominates surface diffusion. This process appears to have an activation energy $Q = 0.24\ \Delta H_s$, where ΔH_s is the heat of sublimation of the solid. At high temperatures the dominant carriers of the surface diffusion flux are assumed to be ad-atom vacancy pairs with $Q = 0.54\ \Delta H_s$.

For surfaces of body centered cubic solids there is only one surface diffusion mechanism for which $Q = 0.33\ \Delta H_s$, and which is operative throughout the studied temperature range.

ELECTRICAL PROPERTIES OF SURFACES

The concentration of mobile charge carriers (electrons and diffusing ions) can, to a large extent, determine many of the physical-chemical properties of solid surfaces. The concentration of these free charge carriers, however, varies widely for materials of different types.

Under incident radiation or bombardment by an electron beam the surface emits photons or electrons, or frequently both. The emission properties of solid surfaces differ widely, just as their mechanisms of relaxation after excitation by high energy radiation.

The underlying reason for the differences of the conductivity mechanisms and emission properties in the surfaces of the different materials lies in the differences in their electronic band structure. The electronic levels of the atoms in the solid are filled in accordance with the Pauli exclusion principle, which states that each quantum state can be occupied by no more than two electrons of opposite spins. As the electronic levels are filled from the lowest lying state toward the highest, we can arrive at two different conditions at the outermost electronic band: it could either be partially filled or it could be fully occupied. These two different conditions have far-reaching implications in determining the electrical transport properties of the solid and the emission and optical properties as well.

In those electronic bands completely filled with electrons, the application of an external field has virtually no effect on the electron distribution. A crystal, having only bands that are completely filled or entirely empty, is a perfect insulator. The situation is markedly different in the case of a partially filled band. Since unoccupied states are now available, an external field would give rise to a net shift in the electron distribution. The new distribution would be characterized by a nonvanishing average velocity and therefore results in an electric current. The solids which are characterized by half-filled or partially occupied uppermost electronic bands, show metallic conductivity. Thus we see how the electronic band occupancy at the topmost level can determine the

conductivity of a solid and thereby allows us to classify the different solids according to their charge-carrier concentration or carrier mobility.

For many purposes, in analyzing the electrical properties of metal or semiconductor surfaces, we are not concerned with the detailed shape of the electronic bands. One may conveniently represent schematically the electronic bands by straight lines where the potential energy of the electron near the top of the valence band and at the bottom of the conduction band is plotted against distance x through the crystal starting from the surface (x = 0) (Figure 9). The energy gap represents the minimum potential energy difference between the two bands. For a homogeneous crystal the bands may be horizontal as shown in this Figure. We will see that at the surface the bands may vary in energy with respect to their value in the bulk of the solid since the free carrier concentrations at the surface may be different from those in the bulk of the crystal.

The Surface Space Charge

Mobile charge carriers at the surface (electrons or holes) can interact with adsorbed molecules and can participate in surface reactions. The flow of these free carriers toward or away from the surface can establish a potential gradient between the surface and the bulk of the material that may determine the reactivity of the surface. Any accumulation or depletion of charge carriers in the surface with respect to the bulk carrier concentration establishes a static space charge region near the surface.[17] Such a space charge may also be induced by the application of an external electric field or by the presence of a charged layer on the surface, such as adsorbed ions or electronic surface states (to be discussed below) which act as a source or sink of electrons. The height of the surface potential barrier V_s and its distance of penetration into the bulk, x, depend on the concentration of mobile charge carriers in the surface region.

We can obtain the penetration distance of the field, x_s, as a function of the applied potential and more importantly, the charge density in the material, n_e (bulk) (charge/cm^3) as:

$$x_s \approx \left[\frac{\varepsilon \varepsilon_o |V_s|}{e n_e(\text{bulk})}\right]^{\frac{1}{2}} \qquad (23)$$

V_s is the magnitude of the height of the surface potential barrier and e, ε and ε_o are the unit charge, the dielectric constant of the solid and the permitivity of free space, respectively. Thus the higher the free carrier concentration in the material the smaller the penetration depth of the applied field into the medium. For electron concentration of 10^{17}cm^{-3} or larger the surface potential is so small that it is negligible. The field penetration is restricted to distances on the order of one atomic layer or less, because the large free carrier density screens the solid from the penetration of the external field. For most metals almost every atom contributes one free valence electron. Since the atomic density for most solids is on the order of 10^{22}cm^{-3}, the free carrier concentration in metals is in the range 10^{20}- 10^{22}cm^{-3}. Thus V_s and x_s are so small that they can usually be neglected. For semiconductors, or insulators on the other hand, typical free carrier concentrations at room tmmperature are in the range 10^{10}- 10^{16}cm^{-3}. Therefore, at the surfaces of these materials, there is a space charge barrier of appreciable height and penetration depth that could extend over thousands of atomic layers into the bulk. This is the reason for the sensitivity of semiconductor devices to ambient changes that affect the space charge barrier height.

A space charge also exists at the surfaces of solids that exhibit ionic conductivity (NaCl, LiF, etc.) or protonic conductivity (ice, for example).

Let us now investigate the physical parameters that govern the height, shape, the penetration depth of the space charge barrier at the insulator surface. We will assume that in the absence of any space

charge the electron energy levels remain unchanged right to the surface ($x = 0$) in our energy level diagram (Figure 9). However, if the surface region become enriched or depleted of electrons, the energy bands at the surface indicate that it would require less or more energy now to transfer an electron to the conduction band at the surface. These conditions are shown in Figure 10.

The potential at any point is then a function of the distance x only and is determined by the Poisson equation (17)

$$\frac{d^2V}{dx^2} = \frac{\rho}{\varepsilon \varepsilon_o} \qquad (24)$$

where ρ is the charge density at any point in the crystal, i.e., it is the sum of the charges due to the mobile electrons and holes and the static positive and negative charges. In the crystal as a whole, charge neutrality has to be maintained.

There are exact and also numerical solutions of Equation (24), by using different conditions of charge equilibrium.

For small values of the space charge layer, its height decreases exponentially with the penetration distance. The penetration depth, at which the potential barrier height drops to $1/e$ times its surface value V_s, is the so-called effective Debye length, which essentially characterizes the width of the space charge region.

For impurity doped semiconductors the height of the potential barrier V decreases parabolically as the square of the distance from the surfaces where the height of the space charge barrier is V_s. This case corresponds to the so-called Schottky barrier, which is characterized by the dependence $V \approx x^2$.

We have so far considered the space charge layer properties only in the insulating solid, assuming that the surface layer that acts as a donor or electron trap is of monolayer thickness. This is certainly the case for many experimental systems of interest. However, considering the properties of solid-liquid interfaces or semiconductors-insulator contacts it should be recognized that the space charge layer may extend to

effective Debye lengths on both sides of the interface. This is a most important consideration when one investigates the surface properties of colloid systems or of semiconductor-electrolyte interfaces.

How are the height of the space charge barrier at the surface and other properties of the space charge measured? Changes of the conductivity of samples with large surface-to-volume ratio are measured as a function of various ambient conditions. Chemical surface treatments to vary the barrier height are often used; measurements of surface conductance, field effect and surface capacitance are the most common to investigate the properties of the space charge layer.[17]

Electronic Surface States

When the concept of electron bands of solids was introduced, the effect of the surface on the band structure was not considered. The introduction of such a discontinuity as the surface perturbs the periodic potential and gives rise to solutions of the wave equation that would not have existed for the infinite crystal. These are derived by using appropriate boundary conditions to terminate the crystal and are called surface-state wave functions. These wave functions have solutions that predict the presence of electronic energy states localized at the surface. These states can trap electrons or release them into the conduction band. The allowed energy levels of the surface states lie in the forbidden gaps of the bulk band structure.

One important consequence of the presence of electronic surface states is that the electron bands are modified at the surface even in the absence of a space charge or electron acceptor or donor species (such as adsorbed gases). Experimental investigations of the properties of electronic surface states utilize the same techniques used to study the surface space charge. Data from surface conductance, field effect, or capacitance measurements, when compared with predicted values computed by using a suitable model, can yield definitive information about the energy distribution and occupancy of surface states.

Emission and Recombination at Solid Surfaces

If electrons in a solid are excited by high-energy incident radiation, by thermal energy, or by electron impact, several energy transfer processes can take place. The energy may be transferred to one or more electrons which are then emitted from the surface or excited into the conduction band. This primary process is generally followed by secondary, recombination processes by which the system returns to thermal equilibrium. These recombination processes may involve emission of electromagnetic radiation or further electron emission. Since the energy of the incident beam is, in general, absorbed dominantly by surface atoms or in a thin surface layer, both the primary excitation and the recombination process may provide us with a great deal of information about the physical-chemical properties of surface atoms.

First, we focus our attention on emission and recombination mechanisms that involve only valence electrons; these provide us with a great deal of information about surfaces and are frequently investigated by a variety of experiments. Then we will discuss emission and recombination of electrons in deeper-lying electron bands that can also be used to identify surface atoms and explore their electronic structure.

a) Work Function -- The minimum energy necessary to remove an electron from the highest populated electronic energy level of a material into vacuum is called work function, ϕ. The energy distribution of these electrons, $f(E)$, can be approximated by a Boltzman distribution

$$f(E) \approx e^{-\phi/kT} \tag{25}$$

The current density, $j(\text{amp}[\text{cm}^2])$ of electrons leaving the metal surface is given by

$$j\left(\frac{\text{amp}}{\text{cm}^2}\right) = AT^2 e^{-\phi/kT} \tag{26}$$

where $A = 4\pi emk^2/h^3 = 120$ amp/cm^{2}deg^2. This is the well-known Richardson-Dushman equation. The electron flux leaving the surface increases with increasing temperature and decreasing work function. Thermionic emission is the most frequently used method to produce electron beams.

The work function, strictly speaking, is a bulk property -- it depends on the energy distribution of the electrons in the volume of the materials. However, the measured work functions were found to be very sensitive to surface conditions. Work functions measured from different crystal faces of solids of molybdenum or tungsten are different; there is more than 0.3 eV difference in the work function values for different crystal faces. The influence of the surface on the measured "effective work function" is due to the redistribution of the electron density at the crystal surface.[1] Because of the asymmetry of the atomic potential at the vacuum-solid interface, the energy of the electrons can be further lowered by spreading them over a larger area. Thus the free electron at the surface has to overcome an "image potential" in addition to the work function in order to escape from the solid. The term image potential derives from the model used to calculate this effect, which assumes the existence of an equal but opposite charge on the other side of the surface, in vacuum. The electrostatic interaction between the electron and its positive image charge gives rise to the image potential. The image forces are, in general, increased with increasing atomic density in the surface. We find that the high density low index crystal faces have the highest effective work function.

The adsorption of gases or the presence of certain impurities can markedly change the electron density distribution at crystal surfaces. Therefore, it is not surprising that the effective work function can change greatly because of the presence of foreign atoms on the surface. This effect is then used to examine the nature of chemical interaction between the adsorbed gas molecules and the solid surface.

b) Field Electron Emission -- When an electron is emitted from a metal surface as a result of thermal excitation it has to overcome a binding

energy (work function) of a few electron volts magnitude. Although this attractive potential is electrostatic in nature and therefore of long range ($V \approx 1/r$), it is reduced within angstroms from the crystal surface to a fraction of its value in the solid. Thus electric fields of magnitude $E \approx 1$ volt/Å, or in more common units, $E \approx 10^8$ volts/cm, have to be overcome by electrons during the emission process. Therefore, another method of producing electron emission from a solid surface is by the application of a large electric field of 10^7-10^8 volts/cm normal to the surface. The potential energy barrier, which has to be overcome by an electron for it to escape, can be distorted this way and electrons may "tunnel" through to be emitted. Such an intense electric field can be obtained by applying a negative potential of 10^3- 10^4 volts across a small cathode tip with a radius of curvature r of 10^{-5}- 10^{-4} cm since $E \approx V/r$. The current density emitted from the tip is given by

$$j\left(\frac{\text{amp}}{\text{sec}}\right) = \frac{aE^2}{(\phi + E_F)\phi^{1/2}} \exp\left(\frac{-b\phi^{3/2}}{E}\right) \quad (27)$$

where E (volts/cm) and ϕ(eV) are the field intensity and work function of the emitter, respectively, and a and b are constants.[18] Using this effect, Müller has constructed a <u>field emission microscope</u>, which allows one to study the field emission distribution from surfaces. The electrons emitted from the cathode tip are accelerated onto a fluorescent screen (generally at ground potential) where the emission distribution of the tip is displayed with a magnification proportional to the ratio of the screen surface area to the area of the cathode tip (ratio ~ 10^5). The field emission current is exponentially dependent on the work function between the different crystal faces. Therefore variation in the density of emitted electrons from face to face gives a characteristic image of the tip surface sturcture with good contrast.

c) <u>Surface Ionization: Emission of Positive and Negative Ions</u> -- Consider an atom of ionization potential V_{ion} adsorbed on a metal surface of work

function ϕ. If the atom is in thermal equilibrium with the solid it may vaporize as a neutral atom from the surface after acquiring thermal energy equal to its heat of desorption from the metal, ΔH_{des}. The desorption energy necessary to vaporize it as a positive ion, ΔH^{+}_{des}, on the other hand, can be estimated by[19]

$$\Delta H^{+}_{des} = \Delta H_{des} + V_{ion} - \phi \qquad (28)$$

ΔH^{+}_{des} is obtained by summing the energies needed to vaporize a neutral atom, ionize it in the vapor phase, then returning the electron into the metal surface. If $(V_{ion} - \phi)$ is positive the surface atoms are likely to desorb as neutral species since $\Delta H_{des} < \Delta H^{+}_{des}$. However, for systems in which the metal work function is greater than the ionization potential of the adsorbed atom, i.e., $(V_{ion} - \phi) < 0$, the vaporization of ionic species will occur preferentially. Thus for studies of surface ionization, high work function metals (W, Pt) and adsorbates with low ionization potentials (Cs, Rb, K) are utilized.

The degree of ionization, the ratio of ion flux j_+ to the flux of neutral atoms j_o desorbing from the metal surface, is given by the so-called Saha-Langmuir equation

$$\frac{j_+}{j_o} = \frac{g_+}{g_o} \exp\left[-\frac{e(V_{ion} - \phi)}{kT}\right] \qquad (29)$$

where g_+/g_o is the ratio of the statistical weights of the ionic and atomic states.

In addition to alkali metals, alkali-halides (NaCl, LiF, etc.) and alkali earth metals atoms (Ba, Mg, etc.) have also been ionized by surface ionization. Tungsten and platinum surfaces are used most frequently in these studies since platinum, in addition to its chemical inertness to most of the adsorbates, has a higher average work function [$\bar{\phi}$(Pt) = 6.35 eV] than does tungsten [$\bar{\phi}$(W) = 4.52 eV].

The emission of negative ions has also been observed under conditions of surface ionization. If the electron affinity S of a negative ion is defined by the reaction $A + e \xrightarrow{S} A^-$, the desorption energy of negative ions, ΔH^-_{des}, can be estimated by[19]

$$\Delta H^-_{des} = \Delta H_{des} + S + \phi \qquad (30)$$

If $(S + \phi) < 0$, i.e., the electron affinity is negative and of greater magnitude than the work function (which is always positive) the atoms adsorbed on the metal surface are most likely to desorb as negative ions. The degree of ionization is given by the equation

$$\frac{j_-}{j_o} = \frac{g_-}{g_o} \exp\left[-\frac{(S + \phi)}{kT}\right] \qquad (31)$$

which is similar to Equation (29).

d) Field Ionization -- The first ionization energy of free atoms of most elements in the periodic table is in the range 3-25 eV. Therefore, just as for an electron in a solid, a valence electron in a free atom has to overcome an electric field on the order of $E \approx 10^8$ volts/cm to be removed from the present positive ion to infinity. If we can apply an electric field of the same order of magnitude at a metal tip we should be able to ionize free atoms of all kinds that approach the surface. For field ionization, however, the surface should be charged positively in order to repel the ions formed at the surface.

The geometry of a field ion microscope is similar to that of a field emission microscope. The ionizing gas most recently used in these studies is helium. The helium atoms ($V_{ion} = 24.47$ eV) present at pressures between 10^{-4}-10^{-3} torr are ionized at the field emission tip (now at positive potential with respect to the screen which is grounded) using fields on the order of $E \approx 10^8$ volts/cm. The electric field strength at the surface is modulated by the atomic structure. This variation, in turn,

modulates the ion current density leaving from the proximity of different crystal faces that make up the emitter. The positive ions are then repelled and accelerated onto the fluorescent screen where the greatly magnified image of the tip surface is displayed. Although the process is similar to that which gives the image of the surface in field electron emission, the use of ions instead of electrons to form the image of the tip increases the resolution markedly. Due to the larger mass there is little displacement of ions along the surface of the tip (tangential displacement) as compared with electrons, during their residence time at the emitter. Tangential displacement could introduce uncertainty in the ion position and therefore, blurring of the image.

e) Recombination Processes and Oscillation of Valence Electrons -- When an electron in an insulator or semiconductor is excited by thermal energy transfer (electron impact or electromagnetic radiation) across the band gap into the conduction band it remains there until it loses its energy by some kind of de-excitation prcoess.[20] De-excitation may take place in several ways. (1) Direct band-to-band transitions. If this recombination process dominates, electromagnetic radiation of band-gap energy is emitted. This radiative recombination is characteristic of many compounds in the II-VI and III-V groups in the periodic table. Many of these diatomic solids are used as light-emitting phosphors in cathode-ray tubes (oscilloscope screen or television screen, etc.) if the band-gap energy is in the range of visible light energy (for example, ZnS and CdS). Phosphors that emit in the infrared are also widely utilized (GaAs, GaP, and InSb). Photon emission may also take place if (2) recombination occurs via impurity centers. For example, thallium-doped sodium iodide crystals are presently used as scintillation counters.

There are other indirect de-excitation processes. The electron energy can be transmitted to the crystal lattice as a whole via (3) excitation of lattice vibrations (phonon emission). The transfer of energy to the crystal requires the excitation of many phonons since the lattice vibration energies are much small than the electron energy to be transferred. The solid will

frequently heat up because of this process. (4) The electron that recombines may also transfer its energy to another electron in the conduction band which may then be emitted from the solid (Auger process). Since Auger transitions are among the most probable characteristic energy-loss processes that take place during excitation by an electron beam, they can be conveniently used to analyze the surface composition and to identify surface impurities.

In a solid the nearly free electrons are known to oscillate with a characteristic frequency ω_p, called plasma frequency, which depends on the electron density. This collective oscillation of the electrons can be detected by the characteristic energy loss of an electron beam, $\Delta E = h\omega_p$, which is transmitted through a thin film of the solid.

"Surface plasmons," which oscillate with a frequency that is less than the characteristic bulk plasma frequency ω_p, have been detected from the characteristic loss spectrum of the electron beam, which was studied as a function of incident angle.(1) Since the surface plasma frequency is sensitive to chemical changes at the surface (oxidation or presence of impurities) and surface roughness, its study provides a great deal of information about a variety of important surface properties.

f) Photoelectron and Auger Electron Emission -- When a high energy electron beam (10^3-10^5 eV) or high energy electromagnetic radiation (x-ray) is allowed to strike the solid surface in addition to electron emission from the valence band, electrons are excited from inner electron shells as well.(21) An electron may be ejected from the K shell into vacuum. For sodium, for example, the minimum energy required for this process is 1072 eV. If the energy of the incident radiation is greater than the binding energy of the electron, this process, which is commonly called "photoelectron emission," can take place. From the knowledge of the incident beam energy and by suitable analysis of the ejected photoelectrons,

the electronic binding energies in the different bands can be obtained. On the other hand, the electron may only be excited into the conduction band of an insulator or just above the Fermi level in a metal.

Energy analysis of the emitted photoelectrons is called photoelectron spectroscopy; the energy analysis of the absorption peaks is called x-ray absorption spectroscopy. In general the photoelectron spectra give peaks of higher intensity and better energy resolution (commonly ± 1 eV) than the absorption spectra.

Let us now turn our attention to the dominant recombination or de-excitation processes which follow the excitation of electrons from inner shells. The first mode of de-excitation is the Auger process (Figure 11), which leads to further electron emission. The second type involves the emission of electromagnetic radiation and is commonly called x-ray fluorescence. In the Auger transition the electron vacancy (in the K shell, for example) is filled by an electron from an outer band (L_I shell). The energy released by this transition is transferred to another electron in one of the electron levels (L_{III} shell) which is then ejected. Energy analysis of the emitted electrons will give differences in binding energy between electronic bands participating in the Auger process (KL_IL_{III}) that are characteristic of a given element.

In recent years Auger electron spectroscopy and photoelectron spectroscopy have come to play dominant roles in studies analyzing the composition of surfaces.[22] When the excitation of Auger transitions is carried out by an electron beam under a grazing angle of incidence, most of the Auger electrons are the products of electronic transitions in the topmost atomic layer. Thus this technique can conveniently be used to determine nondestructively the composition of the surface and changes of the surface composition under a variety of experimental conditions. Since the Auger transition probabilities are large, especially for elements of low atomic number, surface impurities in quantities as little as 1% of a monolayer ($\sim 10^{13}$ atoms/cm^2) may be detected. In photoelectron spectroscopy, x-ray excitation is used in most studies to produce photoelectrons even though electron beam excitation could be of advantage in surface studies.

Although the incident x-ray beam penetrates deeper into the solid than an electron beam of similar energy would, most of the photoelectrons ejected must be generated near the surface to be able to leave the crystal. Therefore their energy analysis under suitable conditions can provide surface chemical analysis.

In addition to the detection of elemental chemical composition, photoelectron spectroscopy can distinguish between the different oxidation states of elements, because of a shift in the binding energies of inner shell electrons upon the change of valency.[21] This is commonly called the chemical shift. For example, the binding energy of beryllium-1s electrons shifts to higher values by about 2.9 eV upon oxidation.

By monitoring chemical shifts, photoelectron spectroscopy has not only been able to distinguish between different oxidation states but also to detect other changes in the chemical environment that lead to the redistribution of the electron density. It could differentiate between BeO and BeF_2 for example. Carbon atoms that are surrounded by hydrogen atoms (methyl group) or are part of a carboxyl group are also distinguishable. Thus analysis of complex organic compounds with direct identification of the different constituent groups from their different chemical shifts became possible.

Auger spectroscopy can also be used to analyze the oxidation state or the changing electronic environment of surface atoms as indicated by the chemical shifts of the characteristic Auger peaks. Since the chemical shifts of the Auger transitions have been detected only recently, experimental data have not been available to such an extent as in photoelectron spectroscopy. Nonetheless it is expected that chemical shifts will be used to distinguish between surface and bulk atoms and to monitor the changing chemical environment of surface species.

STUDIES OF GAS-SURFACE INTERACTIONS

Surface studies are very sensitive to ambient contamination. Thus surface chemists are continually faced with the problem of cleaning their surfaces carefully before starting an experiment either by working in high vacuum or using freshly prepared interfaces (by cleavage for example). Virtually any investigation in surface chemistry also involves the consideration of the interaction of gas molecules with the surface of the condensed phase.

The experimental measurements used in studies of the elementary steps of gas-surface interactions can be divided into two classes: 1) those which provide information about the energy transfer in gas-solid interactions on an atomic scale and 2) those which monitor the overall adsorption process and the properties of the adsorbed layer to yield macroscopic experimental parameters.

We will divide gas-surface interactions into two types, weak and strong interactions, and discuss them separately. Then, we will discuss the structure, the thermodynamic and electrical properties of the adsorbed layer.

A gas atom or molecule "feels" an attractive potential upon approaching surfaces of different kinds. The "strength" of this potential determines the nature of the interaction between the gas and the surface atoms. The strength of the interaction can be expressed in terms of experimentally measurable parameters in several ways. The integral heat of adsorption, ΔH_{ads}, is the average binding energy per mole (average heat of adsorption) between the interacting gas atoms and surface atoms. ΔH_{ads} is related to the depth of the potential energy well for the gas atom adsorbed on the surface, and can be obtained from adsorption or desorption studies.

The ratio of the well-depth of the interaction potential and the thermal energy of the gas atoms at the surface, $\Delta H_{ads}/RT$ determines the residence time of the gas atom on the surface. The residence time τ may be estimated by[23]

$$\tau = \tau_o e^{\Delta H_{ads}/RT} \qquad (32)$$

where τ_o can be related to the period of surface-atom vibration. Measurement of the residence time can also give one an estimate of the type of interaction that takes place between the gas and the surface.

Frequently, the "range" of attraction of the interaction potential between the gas and surface atoms is used to describe the nature of the interaction. The potential energy of attraction is short range, if it decreases inversely as some large power of the distance between the gas and the surface atoms (r^{-3}, r^{-6}). There are gas-surface interactions, however, characterized by electrostatic potential energy that varies inversely with the first power of the gas-surface distance and usually involves direct charge transfer or charge sharing between the colliding gas atom and the surface atom. Such an interaction potential is long range and leads to strong interaction. Experimental determination of the range of the gas-surface interaction is difficult and has been carried out only for a few systems.(1)

Atomic and Molecular Beam Scattering Studies From Surfaces

In these experiments a "beam" of gas atoms that is monoenergetic or has a well-defined velocity distribution is allowed to strike a surface (preferably a single crystal with known temperature, orientation, roughness, etc.) at a given angle of incidence. The flux, velocity, and/or the density of the scattered beam is detected as a function of scattering angle (angular distribution) by using a detector (usually a mass spectrometer or ion gauge). From the properties of the incident beam (velocity, direction), the surface, (temperature, atomic weight, orientation, etc.), and the scattered beam (velocity, angular distribution, etc.), the dynamics of the gas-surface interaction can be determined.

Different phenomena may occur during the collision of gas atoms with surface atoms: a) the gas atoms may diffract from the surface (elastic scattering), b) the gas atoms may exchange a small amount of energy with the surface (weak inelastic scattering) or c) the molecules strongly interact with the surface which often leads to chemical reaction.

a) Diffraction of gas atoms by surfaces -- We can calculate the wavelength associated with the atoms by using the de Broglie equation

$$\lambda = \frac{h}{(2M\bar{T})^{1/2}} \qquad (33)$$

where $\bar{T}$ is the kinetic energy of the atoms. For a thermal helium beam $\lambda \approx 1$ Å so that diffraction of these gas atoms from a row of surface atoms is possible.

Diffraction of helium from cleaved (100) surfaces of lithium fluoride crystals had been detected by Estermann and Stern in 1939, and their experiement has been repeated and verified more recently. Diffraction of helium beams from metallic (silver) surfaces has also been attempted but so far

(next page)

without success. Experimental difficulties may have been the cause of the lack of success. It has been proposed that the large free electron density at metal surfaces and the large Debye-Waller factor for surface atoms modify the surface potential "felt" by the incident helium atom so as to minimize its periodic nature. Clearly, more diffraction experiments have to be carried out on a variety of solid surfaces to further explore the nature of atomic beam diffraction.

b) Weak Inelastic Scattering of Gas Atoms from Surfaces -- The energy associated with lattice vibrations is of the same magnitude as the kinetic energy of the incident atomic beam. Therefore, direct energy transfer between the incident beam and the surface can take place, which could markedly alter the angular and energy distribution of the scattered atomic beam. Indeed, a large fraction of the incident atoms undergoes inelastic scattering with the surface. If the surface temperature, T_s is smaller than the temperature associated with the gas atoms, T_g, part of the kinetic energy of the gas atom may be transferred to the surface during the collision. For $T_s > T_g$, energy transfer from the surface to the gas atom is likely to take place.

There have been several calculations to describe the dynamics of weak gas-surface collisions. The "hard-cube" scattering model [24] leads to a closed form expression of the angular distribution of the scattered beam. In the model for weak interactions the gas and surface atoms are assumed to be rigid elastic particles. The surface is assumed to be perfectly smooth and the surface atoms are represented by one-dimensional harmonic oscillators that can move only normal to the surface and which are confined by independent square-well potentials. The change of angle reflects the change of momentum of the gas atom during collision with the surface. In the hard-cube scattering model the tangential velocity of the gas atom (i.e., velocity component along the surface) is assumed unchanged by the collision because no forces act parallel to the surface.

In most atomic beam scattering experiments the experimental data are obtained by monitoring the scattered beam intensity I as a function of scattering angle ϕ while keeping the other variables such as the incident angle, θ, the surface and characteristic gas temperatures, T_s and T_g, and the atomic weights of the gas and the surface, m and M, constant.

In general, the scattered beam has a lobular distribution with a maximum at a characteristic scattering angle ϕ_{max} (Fig. 11). The hard-cube scattering theory predicts well the dependences of ϕ_{max} on the variables, m, M, T_s, T_g, and θ.

Accommodation coefficients -- Frequently one is more interested in determining the energy distribution of the scattered beam than in measuring its angular distribution. To this end, one may define an energy accommodation coefficient α_E, as

$$\alpha_E = (E_i - E_r)/(E_i - E_s) \qquad (34)$$

where E_i and E_r are the kinetic energies of the incident and reflected atomic beam, respectively, and E_s is the mean energy of the gas atoms at the surface temperature, T_s. The energy accommodation coefficient so defined takes up values between 0 and 1. If there is no energy exchange between the gas and the surface, $E_i = E_r$ and $\alpha_E = 0$. For complete energy accomodation on the surface, $E_r = E_s$ and $\alpha_E = 1$.

Usually the limited energy exchange between the gas and the surface are studied by thermal accommodation experiments (rather than by the more difficult molecular beam techniques). In these investigations one determines the thermal energy of the gas (i.e., gas temperature change) before and after the partial energy exchange with the surface. The thermal accommodation coefficient is commonly defines as

$$\alpha(T) = \frac{T_g - T_g'}{T_g - T_s} \qquad (35)$$

where T_s is the surface temperature and T_g and T_g' are the temperatures associated with the gas before and after scattering from the surface, respectively. Equation (35) is similar to the definition of the energy accomodation coefficient, Equation (34).

It is important to consider the effect of surface impurities on the thermal accommodation coefficient of a gas. Light adsorbed impurity atoms for which the atomic mass is smaller than that for atoms in the host lattice

tend to facilitate the energy transfer between the gas and the surface, as shown by experiments. Thus the adsorption of light atoms increases the thermal accommodation coefficient. The presence of heavy impurity atoms, for which the atomic mass is greater than that for atoms in the clean surface, is expected to influence the thermal accommodation coefficient to a lesser extent.

c) Molecular Scattering Studies of Strong Interactions of Gas Molecules with Surfaces--

When gas atoms or molecules that experience a strong attractive potential strike a surface they are likely to stick to the surface for times much longer than lattice vibration times of surface atoms. Complete thermal accommodation of the incident molecular beam can often occur and then the molecules are re-emitted from the surface with angular and energy distributions corresponding to the surface temperature T_s. The flux of molecules that emerges from the surface in a solid angle $d\omega$ at a scattering angle ϕ relative to a surface normal is

$$dF = (d\omega/4\pi)\, n\, \bar{c} \cos\phi \qquad (45)$$

which is the well-known cosine distribution from the kinetic theory.

In most molecular beam scattering experiments, however, there is only partial energy transfer between the surface and the gas molecules. The incident molecules are rescattered from the surface before they can be fully accommodated.

The incident atom or molecule may also undergo strong interaction with the surface which leads to a chemical reaction. Reactive scattering may be divided into two classes: 1) Those that lead to chemical reactions between the gas and the surface in which the surface acts as one of the reactants. 2) Surface chemical reactions in which the incident gas molecule undergoes dissociation or other chemical rearrangements (association, hydrogenation, etc.), but the surface may participate only as a "catalyst" by providing reaction sites, mobile charge carriers, etc., while remaining unchanged structurally and chemically during the reaction.[1]

It should be possible to deduce the energy transfer processes that take place during the strong surface interactions (and reactive scattering) of molecules by monitoring the energy and angular distributions and composition of the scattered beams. So far only a few investigations of this type have been reported.[1] It is hoped that reactive-scattering studies will be carried out in the near future since the understanding of the nature of energy transfer in surface reactions is a problem of great importance in surface science.

Physical Adsorption

We will now concern ourselves with the properties of the adsorbed layer of a weakly interacting gas on a solid surface. We can see from Equation (32) that the residence time of weakly interacting gas atoms can be increased markedly by decreasing the temperature at which the experiment is carried out. Assuming a heat of adsorption $\Delta H_{ads} \approx 2$ kcal/mole, the residence time at 300°K is on the order of 10^{-11} second. At 100°K, however, it is greater than 10^{-7} second. Thus by judicious choice of the experimental conditions we can maintain a larger concentration of gas atoms σ on the surface, even for small values of ΔH_{ads}. It is not difficult to see that in addition to the residence time, the surface concentration or surface "coverage" σ will also depend on the flux of gas atoms, F, striking the surface per unit area per second. The surface coverage is given by the product,[23]

$$\sigma = \tau F \tag{36}$$

The gas flux is proportional to the pressure and the residence time is defined in Equation (32). Thus, we have

$$\sigma = \frac{N_A P}{\sqrt{2\pi MRT}} \tau_o e^{\Delta H_{ads}/RT} \tag{36a}$$

From the knowledge of ΔH_{ads}, p, and T, σ can be estimated.

The gas atoms adsorbed on the surface at a given temperature, T and pressure p are either localized at well defined surface sites or are

mobile (i.e., they possess translational degrees of freedom along the surface). The structure of the adsorbed layer can be studied by low energy electron diffraction. Although the surface structure of adsorbed gases during physical adsorption should provide one with important information about the nature of the adsorbed layer, such studies have been carried out only recently for only a few systems.

a) Surface Structure -- Ordered surface structure of xenon on the graphite surface was observed at -90°K and at 10^{-} torr by low energy electron diffraction. LEED studies have revealed the presence of an ordered argon surface structure on the (110) crystal face of niobium at 20°K. However, LEED studies of the adsorption of several gases (O_2, Ar, Xe, C_2H_4) on the silver single crystals at temperatures 100-270°K indicated that the adsorbed gases are disordered.[5] It is hoped that a great deal of structural information will become available in the near future.

b) Adsorption isotherms and other thermodynamic properties of the adsorbed layer -- Most of our information about the nature of the weakly adsorbed gas layer comes from macroscopic studies of the amount of gas adsorbed on the surface σ (surface coverage), as a function of gas pressure p at a given temperature. The σ-p curves are called adsorption isotherms. The adsorption isotherms are used primarily to determine thermodynamic parameters that characterize the adsorbed layer (heats of adsorption and the entropy and heat capacity change associated with the adsorption process) and to determine the surface area of the adsorbing solid. The latter measurement is of great technical importance because of the widespread use of porous solids of high surface area in various industrial processes. The simplest adsorption isotherm at a constant temperature is obtained from Equation (36a), which we can rewrite as

$$\sigma = k\,p \qquad (37)$$

where $k = N_A(2\pi MRT)^{-\frac{1}{2}}\,\tau_o \exp\,[-\Delta H_{ads}/RT]$. Equation (37) is unlikely to be suitable to describe the overall adsorption process. Nevertheless, it

approximates the adsorption isotherms for many real systems at low pressures ($< 10^{-5}$ torr) and at high pressure (10 torr) at the initial stages of adsorption. For example, the adsorption isotherms of argon on silica gel obey Equation (37).

Langmuir has derived a different adsorption isotherm by assuming that adsorption is terminated upon completion of a monomolecular adsorbed gas layer.[1] If σ_o is the surface coverage in the completely covered surface, the Langmuir isotherm has the form

$$\sigma = \frac{\sigma_o kp}{\sigma_o + kp} \tag{38}$$

By writing $\theta = \sigma/\sigma_o$, where θ is often called the "degree" of covering, Equation (38) can be rewritten as

$$\theta = \frac{k'p}{1 + k'p} \tag{39}$$

where $k' = k/\sigma_o$. Another frequently used adsorption model that allows for adsorption in multilayers where gas atoms or molecules may adsorb on top of already adsorbed molecules, was proposed by Brunauer, Emmett, and Teller[1] (BET). With the exception of the assumption that the adsorption process terminates at monolayer coverage, they have retained all other assumptions made in deriving the Langmuir adsorption isotherm. The BET model leads to a two-parameter adsorption equation of the form

$$\frac{p}{\sigma(p_o - p)} = \frac{1}{\sigma_o c} + \frac{(c - 1)}{\sigma_o c}\,\frac{p}{p_o} \tag{40}$$

where p_o is the saturation pressure of the vapor at which an "infinite" number of layers can be built up on the surface and c is a constant at a given temperature and is an exponential function of the heat of adsorption of the first layer and the heat of condensation or liquefaction of the vapor ΔH_L ($c \propto \exp [\Delta H_{ads} - \Delta H_L] / RT$). A plot of the quantity $p/\sigma(p_o - p)$ vs. p/p_o should yield a straight line with slope $(c - 1)/\sigma_o c$ and intercept $1/\sigma_o c$.

Another useful method of surface area determination was suggested by Harkins and Jura.[11] There appears to be good agreement between the surface areas determined by the Harkins-Jura and the BET methods.

The adsorption isotherm yields the amount of gas adsorbed on the surface, i.e., the product of the average area occupied per molecule and the surface area. Unless the molecular area occupied by the adsorbed gas is known, the adsorption isotherm yields only relative surface areas rather than the absolute values. This is the reason for using only one gas (nitrogen or argon) to determine the surface areas of different solids. However, Harkins and Jura[1] developed an absolute method to determine the surface area of non-porous solids by using an immersion calorimeter. By using this absolute method and the BET or other adsorption isotherms for the same system, the average area occupied by a molecule of a given gas can be obtained. For nitrogen this was found to be 16.2 Å for a variety of surfaces and was adopted as a standard for surface area determinations.

There have been several theoretical models[25] proposed that attempt to give a more realistic description of the gas-surface interactions that lead to physical adsorption than the Langmuir and BET models. The variable parameters in these models are the interaction potential, the structure of the adsorbed layer (mobile or localized monolayer or multi-layer) and the structure of the surface (homogeneous or heterogeneous, number of nearest neighbors). Unfortunately, many of these different detailed models of adsorption yield similar theoretical isotherms. Thus it is essential to obtain supplementary experimental information, in addition to the adsorption isotherms, before a more meaningful theory of physical adsorption can be developed. These experiments involve 1) the determination of the surface structure of weakly adsorbed gases on single crystal surface by LEED, 2) studies of their order-disorder phase transitions by LEED at low temperatures, and 3) determination of adsorption isotherms and the heats of adsorption as a function of coverage for different gases on ordered single-crystal surfaces. So far, such studies have been carried out for only a few systems.

Recently, ellipsometry techniques[1] were found to be useful in measuring adsorption isotherms on single crystal surfaces. From the adsorption isotherms obtained at different surface temperatures the heats of adsorption as a function of coverage could be calculated. Although contamination of the surface by unwanted condensates can be difficult to control, such measurements promise to yield detailed information about the adsorption process and should aid in the development of realistic theoretical models of physical adsorption.

When a single atom or molecule is adsorbed on a clean surface, heat is liberated, i.e., the adsorption process is always exothermic. The total or integral heat of adsorption ΔH_{ads}, measured for the adsorption of N molecules in the overall adsorption process is proportional to the number of adsorbed molecules N and to the heat of adsorption per molecule, q_{ads}:

$$\Delta H_{ads} = N q_{ads} \tag{41}$$

Frequently one is interested in measuring the differential heat of adsorption $(d\,\Delta H_{ads}/dN)_T$, which is the increase in the heat liberated by adsorbing an additional amount of gas, dN. If q_{ads} is independent of the amount of gas already adsorbed on the surface, a condition which is assumed in deriving the isotherms given by Equations (37), (38), and (40), the differential heat of adsorption is independent of coverage and remains constant as a function of coverage. In reality, the heat of adsorption changes with the amount of gas adsorbed on the surface due to the heterogeneity of the surface. Thus it is useful to differentiate ΔH_{ads} with respect to N to obtain

$$\Delta H_{ads}^{diff} = \left(\frac{d\,\Delta H_{ads}}{dN}\right)_T = q_{ads} + N\left(\frac{dq_{ads}}{dN}\right)_T \tag{42}$$

If the differential heat of adsorption ΔH_{ads}^{diff} is measured under isothermal conditions it is commonly called isothermal or isosteric heat of adsorption.[23]

The ΔH_{ads}^{diff} vs. θ curves may be extrapolated to zero coverage to obtain q_{ads}, which is a direct measure of the interaction energy between the gas molecule and the surface. As the coverage is increased the heat of adsorption may increase or decrease because of 1) interactions between the adsorbed molecules and 2) the availability of different surface sites for adsorption on the heterogeneous surface. At high coverages ($\theta \geq 1$) the heat of adsorption approaches the heat of condensation (liquifaction) of the adsorbed gas indicating that the surface forces no longer play an important role in determining the properties of the adsorbed layer. It should be noted that because of the strong attractive surface forces, at low coverages the heat of adsorption may be several times the value of the heat of liquefaction.

In studies of the thermodynamics of adsorbed layers, it is useful for certain systems (for example, in studies of monomolecular surface films on the liquid surfaces) to define the surface pressure Π as

$$\Pi = \gamma_o - \gamma \tag{43}$$

where γ_o is the surface tension of the clean surface and γ is its surface tension in the presence of the adsorbed layer. For insoluble layers, which are dilute and mobile so that they approximate the properties of a two-dimensional surface gas (gaseous film), we can write the two-dimensional equivalent of the ideal gas law[9]

$$\Pi \mathcal{A} = n_s RT \tag{44}$$

The surface pressure due to adsorbed films on a liquid surface may be measured by "film balances" of different types, which measure changes of surface tension due to spreading or compression of the surface films on liquids.[10] Such measurements are of great importance in testing the properties of soap and detergent solutions. Their role as cleaning agents requires that they alter the surface tension of water to facilitate the dissolution of solids of different kinds. Insoluble monomolecular films

or organic acids spread evenly on the surfaces of lakes and reservoirs are often used to reduce the evaporation rate of water by as much as 40% by making vaporization diffusion limited through the surface film. In this way water may be conserved and used for irrigation of arid areas.

Chemisorption

Strong attractive interaction potential between the incident gas and surface atoms may give rise to residence times $> 10^{-2}$ sec. for heats of adsorption ΔH_{ads} greater than 15 kcal/mole. Thus, even for small gas fluxes ($\leq 10^{-6}$ torr), large surface coverages can be obtained at 300°K or at higher temperature. The adsorption of gases that undergo strong interaction with the surface ($\Delta H_{ads} > 15$ kcal/mole) is frequently called chemisorption. An important part of most studies of gas-surface interactions and many chemical surface reactions is to investigate the structural, thermodynamic, and electrical properties of the chemisorbed layer.

a) The surface structure of chemisorbed gases[5] -- The structure of chemisorbed gases has been studied extensively by low energy electron diffraction. LEED studies have shown that chemisorption predominantly yields ordered structures on single crystal surfaces. The surface structure that form depend, to a great extent, on the symmetry of the substrate; the chemistry and size of the adsorbed gas molecule; and, in some cases, the surface concentration of the adsorbate, which may be controlled by the gas partial pressure over the surface.

The experimental data accumulated so far indicate several regularities or trends that are operative in the formation of surface structures of adsorbed gases on high-density crystal planes. It is possible to propose a set of rules that appear to govern the formation of ordered surface structures.[26] It is hoped that the judicious application of these rules to

other substrate-adsorbate systems that have not been studied will allow one to predict the surface structure that should form. These rules, although they are empirical and are formulated from the correlation of existing surface structural data, are nevertheless based on a strong physical chemical foundation. It appears that chemisorption leads to the formation of surface structures that exhibit maximum adsorbate-adsorbate and adsorbate-substrate interactions.

RULE OF CLOSE PACKING -- Adsorbed atoms or molecules tend to form surface structures characterized by the smallest unit cell permitted by the molecular dimensions and adsorbate-adsorbate and adsorbate-substrate interactions. They prefer close packing arrangements.

RULE OF ROTATIONAL SYMMETRY -- Adsorbed atoms or molecules form ordered structures that have the same rotational symmetry as the substrate face.

RULE OF SIMILAR UNIT CELL VECTORS -- Adsorbed atoms or molecules in monolayer thickness tend to form ordered surface structures characterized by unit cell vectors closely related to the substrate unit cell vectors. Thus the surface structure bears a greater similarity to the substrate structure than to the structure of the bulk condensate.

Classes of chemisorbed surface structures[5] a) Chemisorption "on top". Gases may chemisorb on the surface and arrange themselves in different surface structures according to the rules of ordering given above. Adsorption "on top" implies that the chemisorbed reactants or, if they dissociate, the products of dissociation, stay on the surface and will not subsequently diffuse into the bulk to participate in bulk chemical processes. The structure that forms is a two-dimensional arrangement in which the participating atoms or molecules are those of the adsorbed gas and does not include substrate atoms to any large extent. The adsorption of olefins on platinum surfaces or the adsorption of saturated hydrocarbons on nickel surfaces provide good examples for this type of chemisorption.

b) Co-adsorbed surface structures -- LEED studies uncovered some surface structures that would form during the simultaneous adsorption (co-adsorption) of two gases but that would not form during the adsorption of only one or the other gas component. The formation of these mixed surface structures seems to be a general property of adsorbed gas layers on tungsten surfaces.

c) Reconstructed surface structures -- It has been reported from several studies that a strongly exothermic surface reaction, such as the chemisorption of oxygen on nickel or on other metal surfaces, can dislodge the substrate atoms from their equilibrium positions and cause rearrangements of the substrate structure, which is commonly called reconstruction. The reconstructed surface structure is composed of both metal and chemisorbed atoms in periodic arrays. Although changes in the diffraction pattern during chemisorption can be analyzed in several different ways, complementary experimental evidences seem to indicate that reconstruction is the most likely interpretation of the structural changes observed during the oxidation of many metal surfaces. Reconstruction can be easily rationalized by comparing the heat of adsorption of strongly chemisorbed species with the lattice energies of the different substrate metals and semiconductors. If the heats of adsorption and the lattice energies are of the same magnitude, it indicates the formation of chemical bonds between the adsorbed atom and the substrate that are similar in strength to those between the substrate atoms. Reconstruction of the surface may be looked upon as a precursor for oxidation reactions or other chemical reactions that proceed into the bulk; for example, carbide formation via carbon diffusion, or nitridation via nitrogen diffusion into the bulk by a diffusion controlled mechanism. Since reconstruction displaces and rearranges metal atoms on the surface while forming ordered surface structures, these structures may be stable to much higher temperatures than two-dimensional surface structures which are solely due to adsorbed gases.

d) Amorphous surface structures -- It has been found during studies of the adsorption of oxygen on some metal surfaces that chemisorption takes place via the formation of disordered layers. For example, the chemisorption

of oxygen on aluminum surfaces or oxygen on chromium surfaces takes place in such a manner. This is in contrast with the behavior of oxygen on nickel or tungsten surfaces. Although the experimental information presently available is scanty, it appears that those oxide layers that form non-porous resistant surface films form disordered surface structures. The lack of crystallinity of the surface structures may be correlated with the degree of non-porosity of the deposited oxides in future studies.

e) Three-dimensional structures -- As already discussed, reconstruction of the solid surface may occur during the chemisorption of gases that induce exothermic chemical reactions at the surfaces. Reconstruction may be followed by further chemical reactions, which take place in the bulk of the solid. As the surface species diffuse intothe bulk, the chemical reaction is no longer two dimensional but actually involves the species below the surface. In the final stages of oxidation when the second phase (for example, nickel-oxide) is beginning to precipitate, other surface structures may appear that are characterisitc of that of the bulk oxide or some mixture of the metal and the oxide structures. The condensation of second phases can conveniently be followed by low energy electron diffraction because of the streaking of the diffraction pattern by the strain introduced by the phase transformation. Such studies provide us with new information about the formation of bulk phases or bulk phase transformations.

Adsorption isotherms of chemisorbed gases and their heats of chemisorption -- During the chemisorption of gases, monolayer coverages are obtained at very small pressures ($\leq 10^{-6}$ torr) which, until recently, were outside the pressure range of convenient and reliable experimental adsorption studies. Therefore most of the isotherms for chemisorbed gases are determined at high coverages and are often incomplete.[27] Some of the studied gas-solid systems obeyed the Langmuir isotherm but many chemisorption processes did not. Studies of the temperature dependence of the coverage revealed that the differential heats of adsorption decrease with increasing surface coverage, nearly linearly in some cases. The differential

heats of chemisorption of hydrogen on several metals clearly indicate the variation. In most chemisorption processes the heat of adsorption is thought to decrease with coverage because of the repulsive interaction between adsorbate molecules when they are in close proximity to each other. Let us assume that the heat of chemisorption ΔH_{ads}^{diff} decreases as the linear function of the coverage which can be expressed as

$$\Delta H_{ads}^{diff} = \Delta H_{ads} (\theta = 0)(1 - a\theta) \qquad (46)$$

where $\Delta H_{ads} (\theta = 0)$ is the heat of chemisorption at zero coverage and a is a proportionality constant. The resultant isotherm predicts the linear variation of θ with $\ln p$, is called the Temkin isotherm.

Another frequently used isotherm, the Fraundlich isotherm, implies that the heat of chemisorption falls logarithmically with increasing surface coverage $\left[\Delta H_{ads}^{diff} \approx - \Delta H_{ads} (\theta = 0) \ln \theta\right]$. It is of the form

$$\sigma = c\, p^{1/n} \qquad (47)$$

where c and n are constants that depend on T. It should be noted that the predicted logarithmic $\Delta H_{ads}^{diff} - \theta$ relationship cannot be obeyed as θ approaches zero.

The values obtained for the heats of chemisorption are, in general, less reliable than those obtained for the heats of physical adsorption. Since large coverages can be obtained even at very low equilibrium pressures, it is often very difficult to determine the initial heat of chemisorption $\left[\Delta H_{ads} (\theta \to 0)\right]$. In addition, because of the strong adsorbate-substrate and adsorbate-adsorbate interactions, the heats of chemisorption depend markedly on the surface structure of the substrate (distribution of different surface sites) and on the surface coverage. Heats of chemisorption vary widely between 15 and 200 kcal/mole, whereas heats of physical adsorption are all in the range 2 to 15 kcal/mole.

Electrical properties of the chemisorbed layer -- The work function and its small variation from crystal face to crystal face is due to the redistribution of electron density in the surface layer. It can be readily seen that the adsorption of atoms or molecules that cause a further redistribution of the charge density at the surface gives rise to changes of the work function.[28] If the adsorbed atoms are ionized and transfer electrons into the solid surface the work function decreases. Conversely, the formation of adsorbed negative ions increases the work function. Most frequently the adsorbed atoms or molecules are only polarized by the attractive surface forces, and then they may be viewed as dipoles aligned perpendicularly to the surface. If the adsorbed layer has its negative pole outward, the work function of the electrons in the solid (generally metal) surface increases because of the lowering of the free electron density by charge transfer and charge localization in the adsorbed layer. If the positive pole of the polarized adsorbed layer is outward, the work function decreases on account of the excess electron density transferred to the solid. Thus measurement of work function changes on well-defined metal surfaces can give a great deal of information about the nature of adsorption and the type of surface bond that forms between the adsorbed molecule and the surface atoms.

Work-function changes upon chemisorption are measured by a variety of methods.[1] Most of the work-function studies were carried out on polycrystalline surfaces and can be taken as averages of work-function values for the different low-index crystal faces.

There are several trends in the work function data that should be noted. Both hydrogen and oxygen adsorption on metal surfaces appear to increase the work function. The chemisorption of π-bonded organic molecules (olefins for example) decreases the work function. Carbon monoxide, on the other hand, increases the work function of some metals (Fe, Ni, Co, W, Pt), but decreases the work function of the others (Cu, Au, Ag).

It should be mentioned that the adsorption of rare gases, such as Kr, A, and Xe, decreases the work function of various metals. The magnitude of this induced dipole interaction is proportional to the polarizability of the gas atom.

Chemisorption, which always involves charge transfer between the adsorbate and the surface, can readily yield monolayer coverages on a metal surface because of the presence of mobile charge carriers in large concentrations (about one free electron per surface atom). Chemisorption on semiconductor or insulator surface is more difficult, however, because of the scarcity of free electrons (or holes) available for charge transfer (less than one electron per 10^4 surface atoms). As soon as all the mobile charges are transferred from the topmost atomic layer at the surface to the adsorbed gas atoms a space charge builds up at the surface that opposes the further transfer of charges to the adsorbed gas layer. Thus chemisorption becomes limited by the rate of charge transfer to the surface over the surface space charge potential energy barrier V_s. This barrier does not maintain constant height throughout the chemisorption process but increases with increased number of ionized donors (or acceptors). The barrier height is also temperature-dependent and varies as exp $(-eV_s/kT)$.

Let us consider a typical charge transfer limited chemisorption of an electron acceptor atom on the surface of some n-type semiconductor, which combines with an electron supplied by the bulk of the material. As the chemisorption proceeds, a dipole layer is formed that consists of a negatively charged chemisorbed layer and a positively charged space charge region near the surface. The chemisorption rate which become limited by the rate of arrival of electrons from the bulk to the surface over the space charge barrier can be written in an integral form as

$$- b\, n_e = \log t + C \qquad (48)$$

where b and C are constants and n_e is the free electron concentration which can be transferred to the surface. This type of rate law is frequently called the Elovich rate equation.[1] The chemisorption of oxygen on several semiconductor surfaces (Ge, ZnO, CdSe) obeys this rate law. The oxygen uptake rate is exponentially dependent upon the charge concentration at the surface.

According to the "boundary layer" theory,[1] in any surface reaction where electron transfer through a potential barrier is the rate determining

step, one expects the rate to be exponentially dependent on the transferred electron concentration to give the type of rate law which was obtained in Equation (49). In fact, any adsorption mechanism that requires an activation energy ΔE, and for which the activation energy increases with increasing coverage θ ($\Delta E \propto \theta$), may yield a rate equation in the form $\frac{d\theta}{dt} \propto A\, e^{-\theta/RT}$ that gives an integrated rate equation of the form of Equation (48). Thus it is not surprising that the Elovich equation describes the adsorption rate of different gases on a wide variety of solid surfaces.

The importance of the carrier concentration and the type of carriers available at the surface for chemical processes on semiconductor or insulator surfaces is indicated by several studies. For example, the oxidation of propylene to acrolein on cuprous oxide crystal surfaces was found to depend on the mobile-hole concentration at the surface, which could be changed by variation of the partial pressure of oxygen over the solid.(1)

The surface chemical bond -- From past and recent results of chemisorption studies a consistent physical picture of chemisorption seems to emerge. Chemisorption involves charge transfer between the adsorbate and the substrate. The nature of the chemical bond of the chemisorbed gas depends partly on the properties of the single substrate atom and partly on the structure of the substrate surface. A comparison of the chemistry of chemisorbed gases on metal surfaces with the chemistry of metallo-organic compounds for which the single atom chemical properties are dominant should provide us with a great deal of information about that component of the surface chemical bond that is determined by interaction with a single metal atom. Extension of studies of the surface structures of chemisorbed gases on various single crystal surfaces, their variation with surface coverage and temperature, should aid in exploring the surface structure dependence of the surface chemical bond.

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Figure Captions

Fig. 1 Optical microscope picture of the basal plane of cadmium sulfide at 100x magnification.

Fig. 2 Electron microscope picture of the basal plane of zinc at 10^5x magnification.

Fig. 3 Model of the heterogeneous surface depicting the different surface sites; terrace, kink, ledge, vacancy, ledge-adatom and adatom.

Fig. 4 Field ion emission pattern of a tungsten tip image with helium at 12°K.

Fig. 5a Scheme of the low energy electron diffraction technique.

Fig. 5b Low energy electron diffraction pattern of the (111) face of a platinum single crystal. Incident electron beam energy is about 120 volt.

Fig. 6a Diffraction pattern from the (111) crystal face of silicon that exhibits the (1x1) surface structure.

Fig. 6b Diffraction pattern from the (111) crystal face of silicon that exhibits the (7x7) surface structure.

Fig. 7 A section of a bubble surface with internal and external pressure p_{in} and p_{ext} and surface tension, γ.

Fig. 8 Definition of the contact angle at the solid-liquid interface.

Fig. 9 The energy level diagram as a function of distance, x, from the surface (x=0).

Fig. 10 Energy level diagrams for an intrinsic semiconductor in the presence of a) electron donor or b) electron acceptor surface states.

Fig. 11 The angular distribution of He, Ne, A and Xe atomic beams scattered from oriented Ag (111) films.

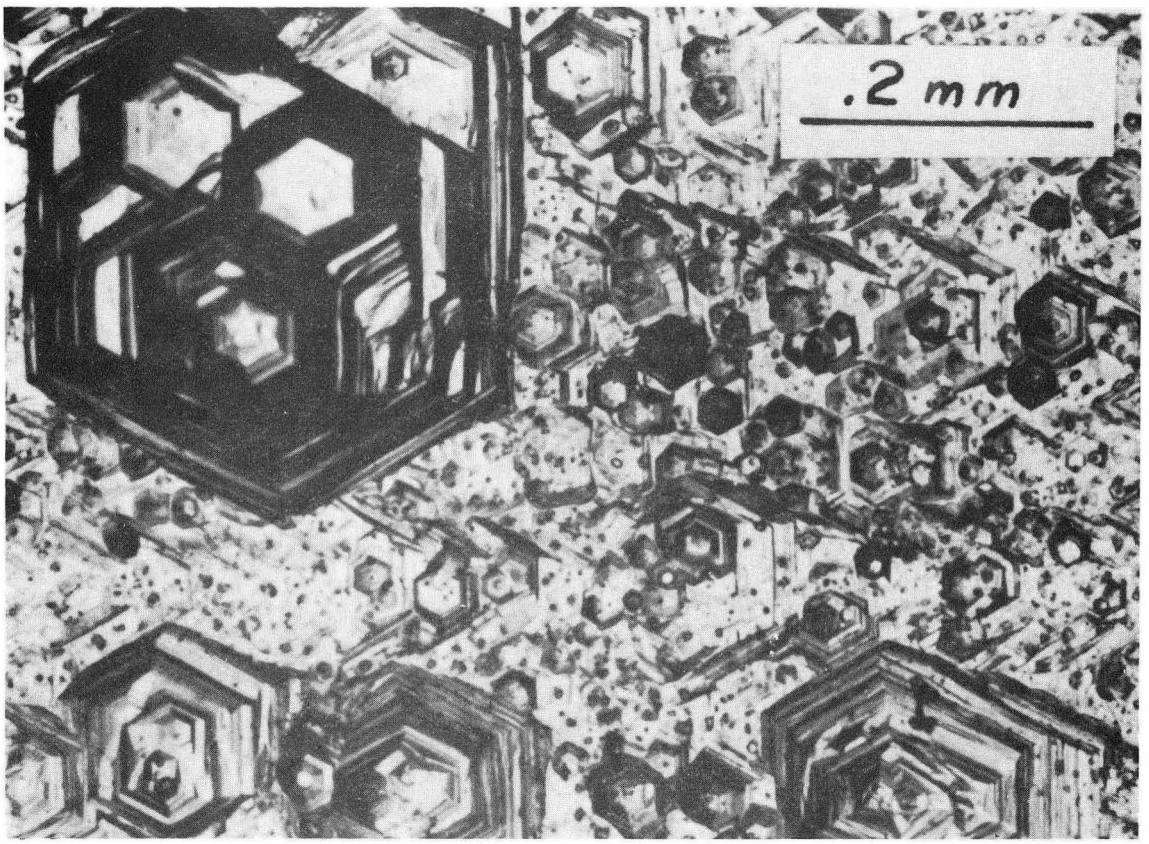

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Fig. 1

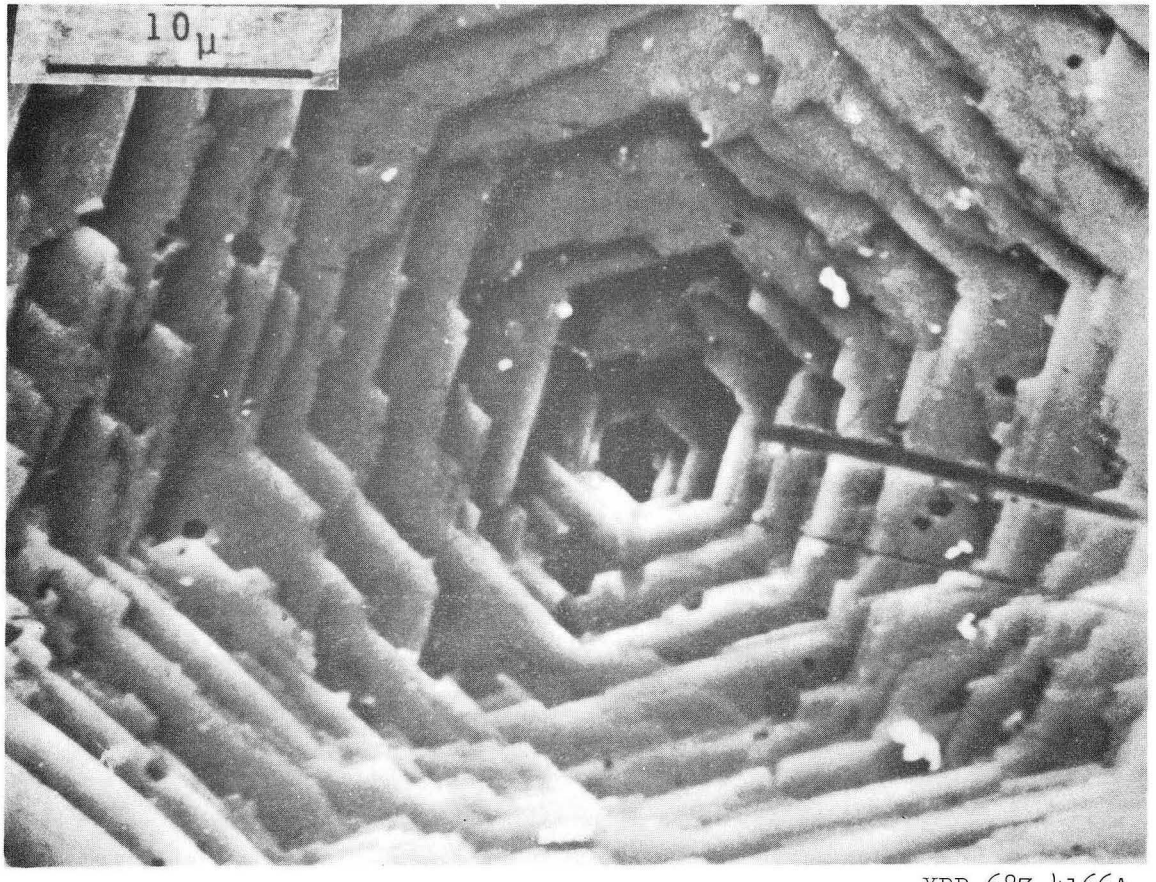

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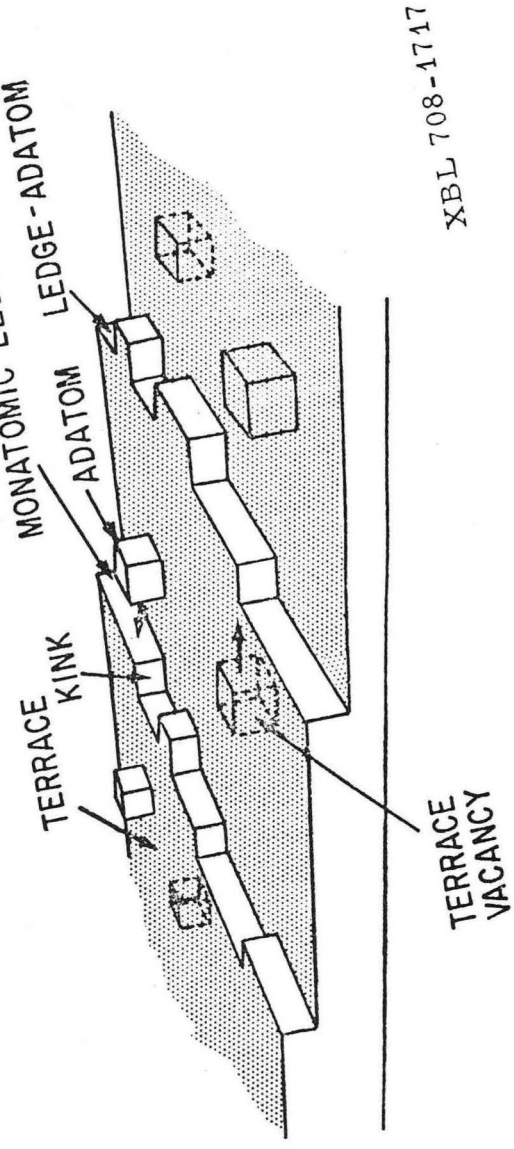
Fig. 2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MONATOMIC LEDGE
ADATOM
KINK
TERRACE
TERRACE VACANCY
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Fig. 3

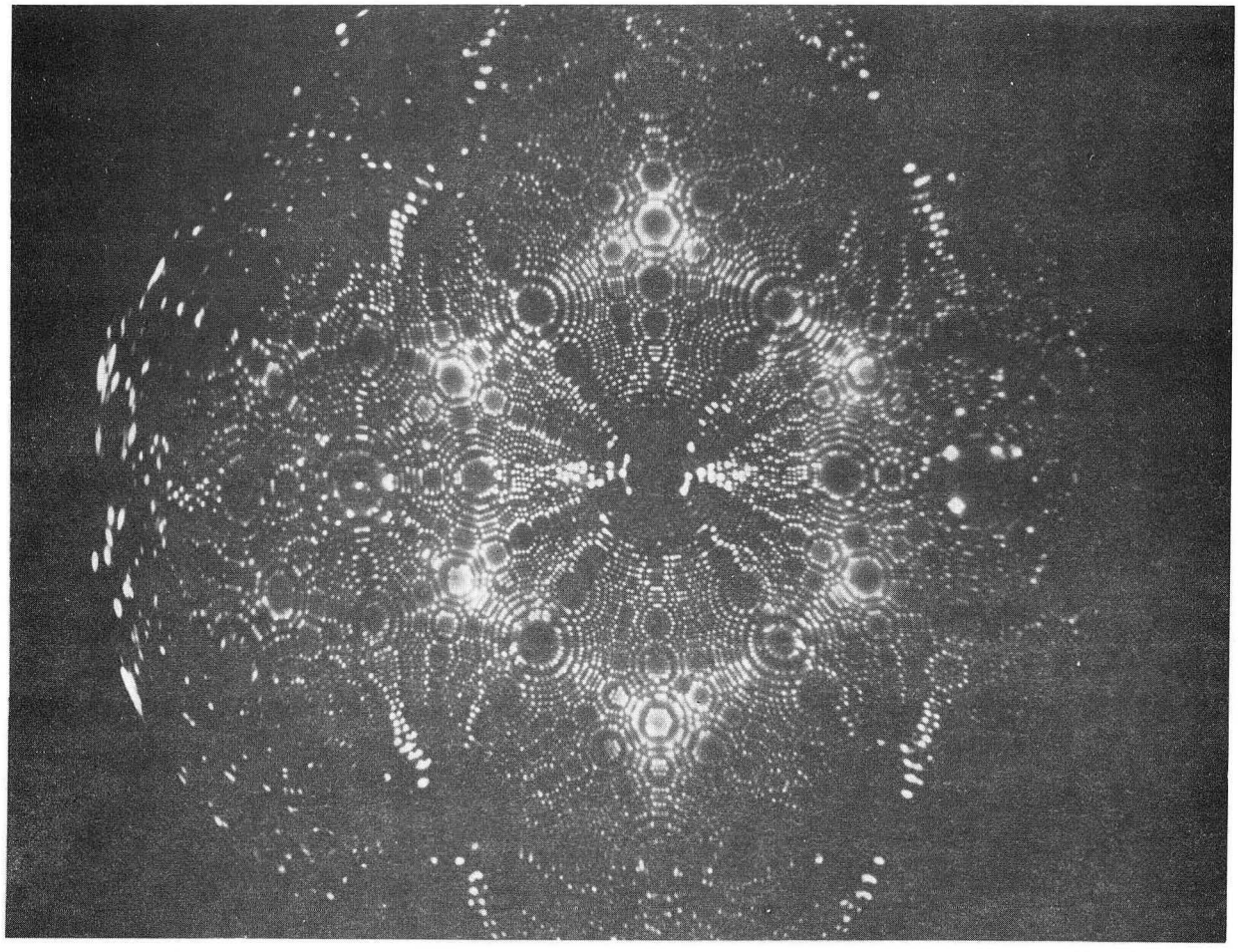

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Fig. 4

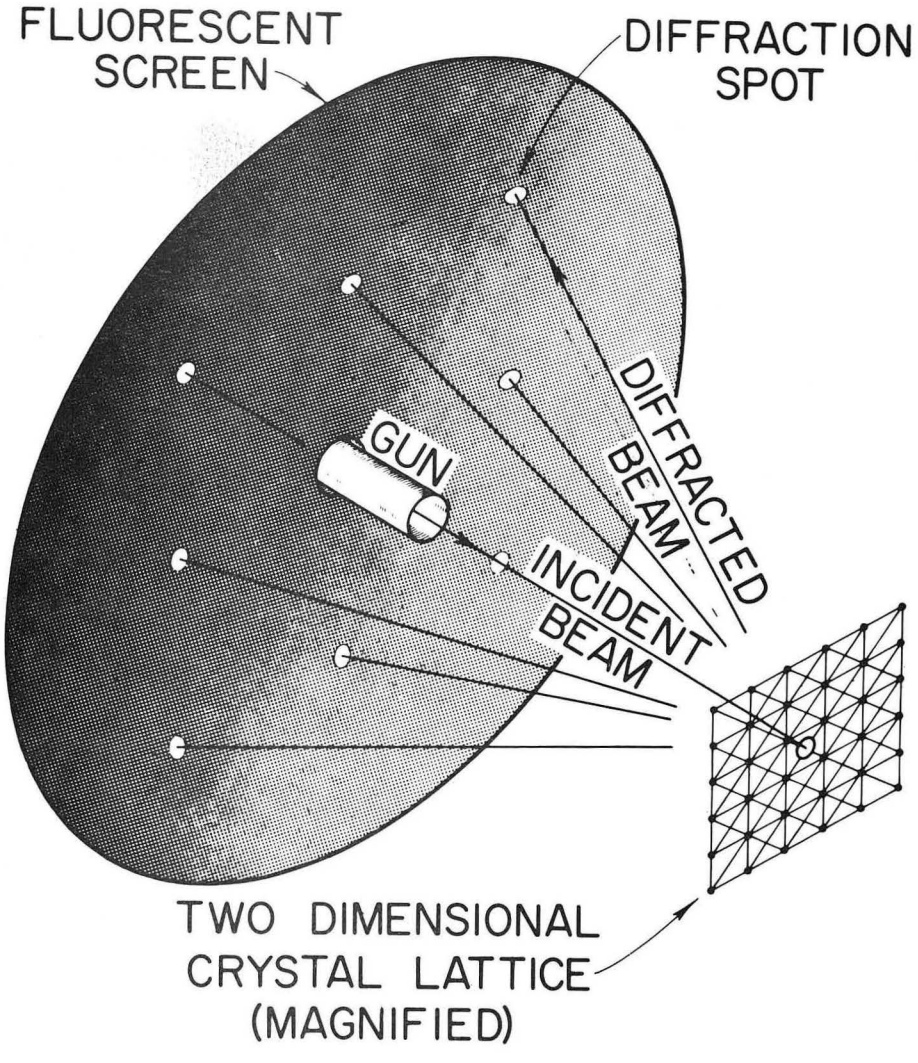

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Fig. 5a

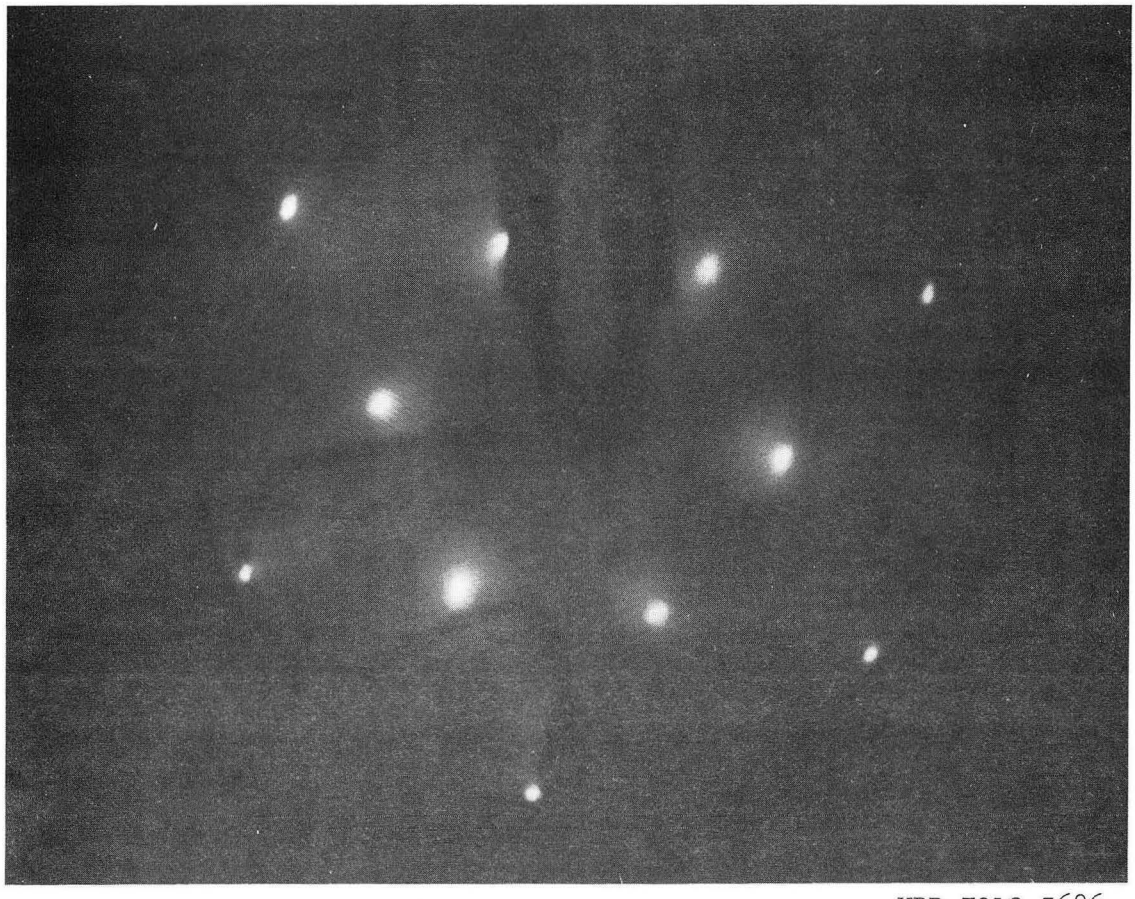

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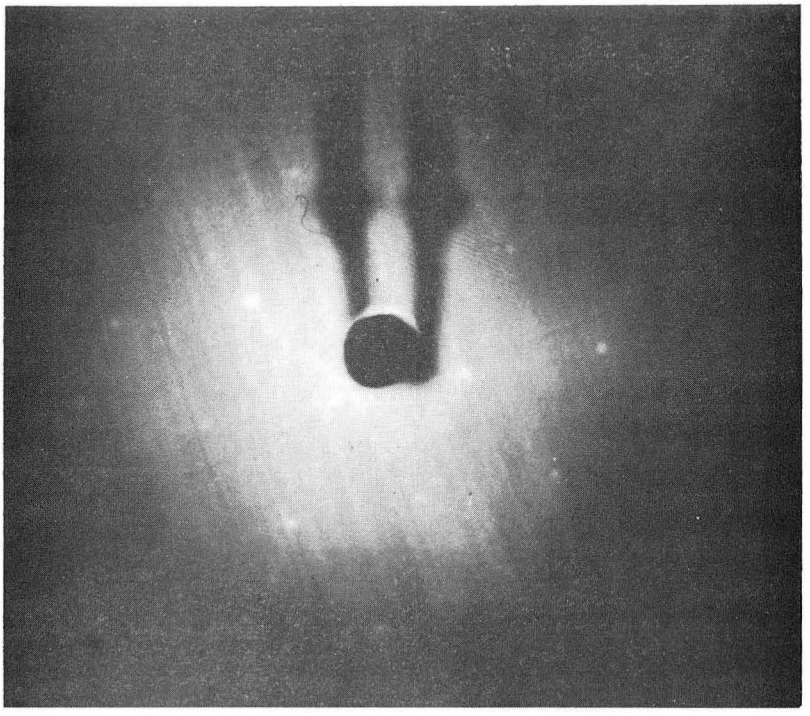
Fig. 5b



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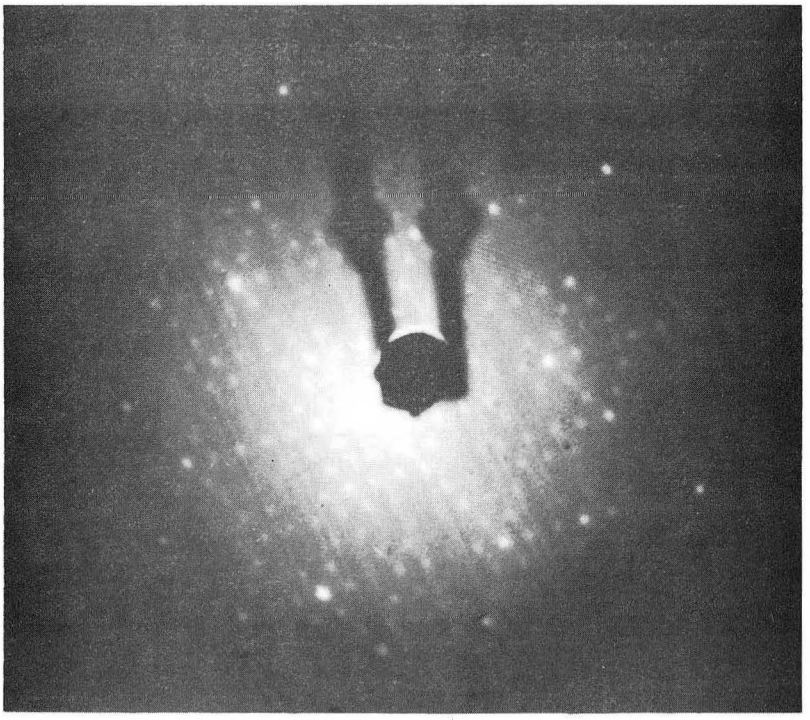

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(b)

Fig. 6

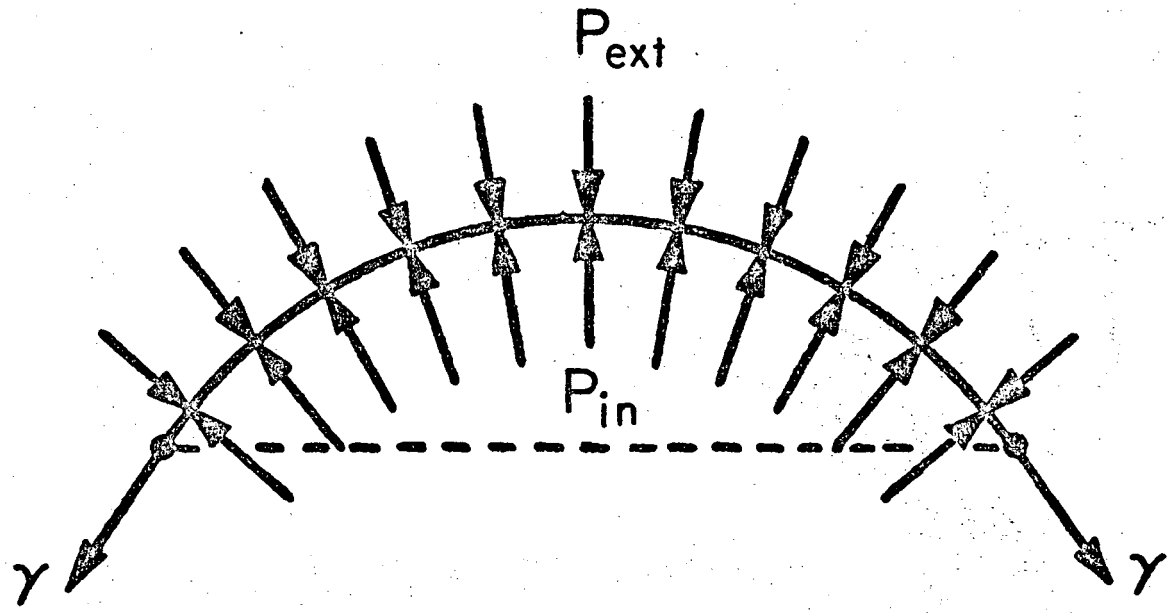

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Fig. 7

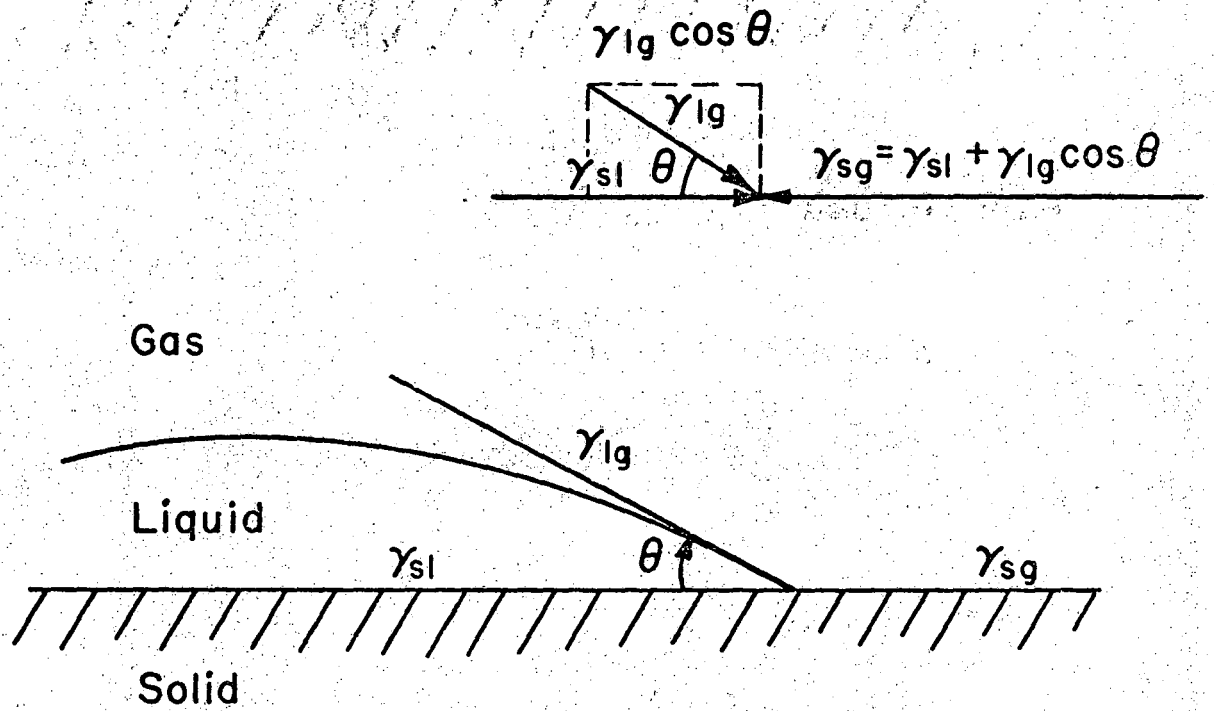
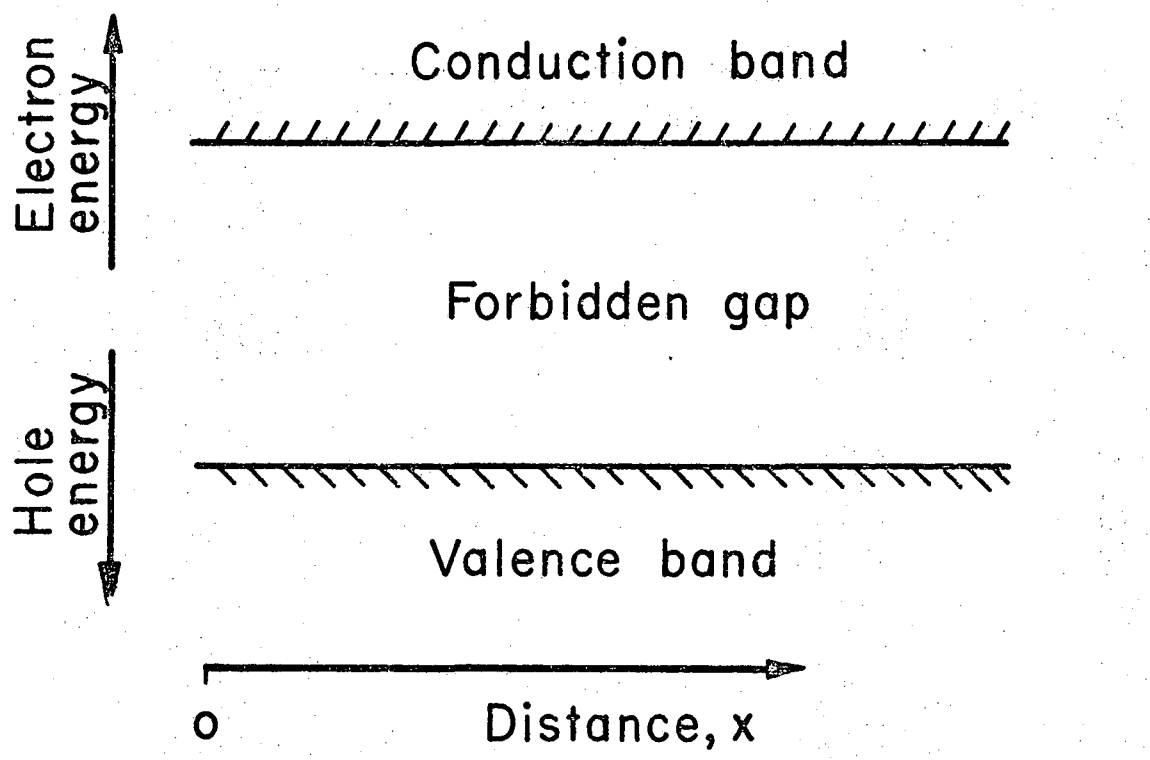

$\gamma_{lg}\cos\theta$
γ_{lg}
γ_{sl}
θ
$\gamma_{sg}=\gamma_{sl}+\gamma_{lg}\cos\theta$
Gas
γ_{lg}
Liquid
γ_{sl}
θ
γ_{sg}
Solid
XBL707-3426

Fig. 8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Conduction band
Forbidden gap
Hole energy
Valence band
o
Distance, x
XBL707-3369

Fig. 9

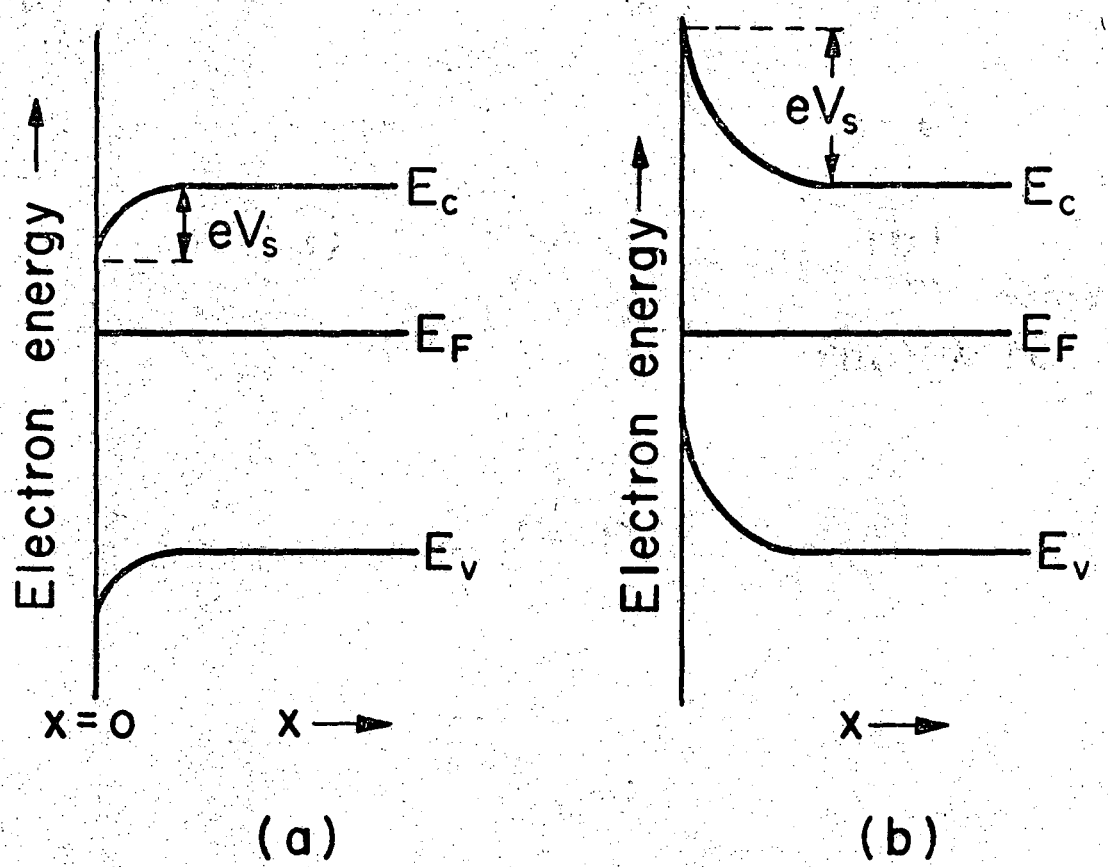

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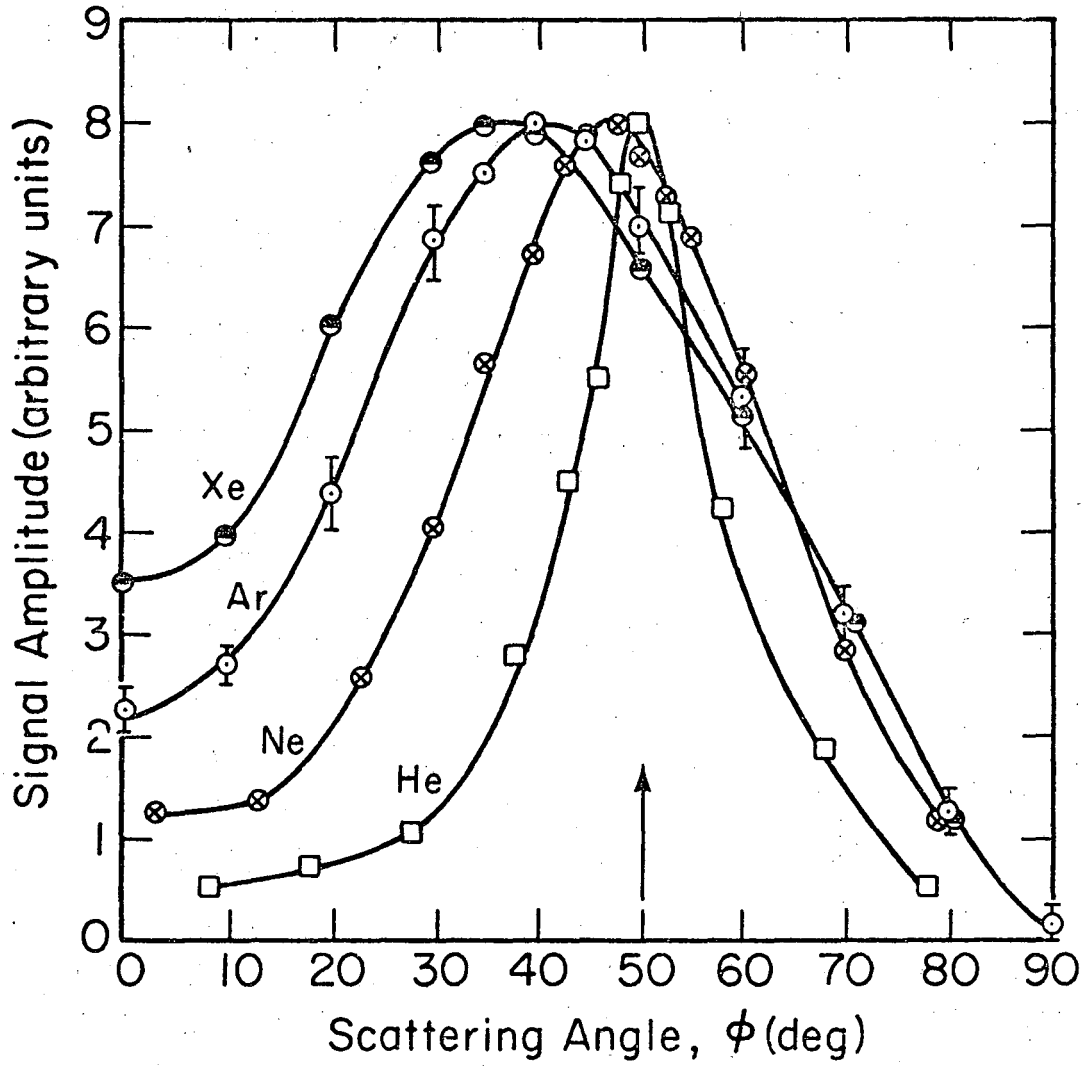
Fig. 10



XBL 708-6407

Fig. 11

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