have said nothing about the strategic value of such a system. The interested reader may wish to examine the arguments put forth by Scoville (*30*), who points out that a demonstrated ability to retaliate is the clue to a stable strategic balance. The specter of the Sanguine project has raised the ire of environmentalists and conservationists in Wisconsin. The environmental aspect is not the subject of this article, but it is safe to say that the envisaged field strengths, even within 100 km of the antenna, will not be harmful, although it may be necessary to mitigate interference with power and communication lines. This subject was discussed at the Newport symposium (*29*).

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Electronic Characterization of Solid Surfaces

Determination of the energy levels of electrons at surfaces is now possible over a wide energy range.

Homer D. Hagstrum

The essentially two-dimensional surface of a solid may reasonably be thought of as a distinguishable phase of matter. Although attached to a bulk solid, its characteristics may depart considerably from those of a simple termination of the solid lattice. When certain strongly bound foreign atoms, for example, are present on a surface, the surface can resemble an ordered array of molecule-like structures. On the other hand, weakly held adsorbates will, at sufficiently high temperatures, be very mobile over the surface.

This is a time of increasing interest in fundamental studies of surfaces. Many new experimental tools needed for the basic characterizations of solid surfaces have been devised within the last decade. Such an increase in surface studies is clearly justified since many phenomena which occur at solid surfaces are of very great importance to mankind. Heterogeneous catalysts, corroding solids, as well as many solid-state electronic devices and biological systems will be understood in a fundamental way only insofar as we understand basic surface phenomena. Furthermore, the conceptual structure that is emerging from basic surface studies, in addition to specific facts, should be of great value in the characterization of more complicated phenomena in which solid surfaces play an important role.

Surface Definitions and Terminology

The surface of a solid may be defined as the outermost atomic layer including foreign atoms absorbed into it and those adsorbed to it (Fig. 1). The surface is attached to what has been called the selvedge (*1*). This is the near-surface region of the solid, and it differs from the deeper, bulk solid by virtue of its proximity to the surface. According to common nomenclature, the attachment of a foreign atom to the surface monolayer of which it is not a part is termed surface adsorption. I shall use the term surface absorption to mean the incorporation of the foreign atom into the surface monolayer either substitutionally where it replaces an atom of the host lattice, or interstitially, where it lies between but in approximately the same plane as the surface substrate atoms. Moreover, foreign atoms can be absorbed into the selvedge or bulk either substitutionally or interstitially as shown in Fig. 1. The atomic "traffic" in both directions between surface and selvedge is often very important in surface studies.

If one views a surface face-on, its two-dimensional structure becomes apparent. In Fig. 2 the surface atoms of the (100) face of a face-centered cubic crystal are shown as open circles. The

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face is made up of a net of square unit meshes labeled (1 × 1) in Fig. 2. Foreign atoms, shown by crossed circles, may lie above the surface monolayer (larger crossed circles) or be incorporated or absorbed into the surface monolayer (smaller crossed circles). The repeat patterns of foreign atoms in Fig. 2 all have a unit mesh twice the size of the (1 × 1) mesh of substrate surface atoms. These so-called (2 × 2) meshes are said to be centered, c(2 × 2), if the mesh has a foreign atom at its center, or primitive, p(2 × 2), it it does not. The adsorbed atom may occupy several possible positions with respect to the substrate atoms of the surface monolayer. As examples, in one arrangement the adsorbate atom lies directly above the substrate atom; in another it lies over the center of the (1 × 1) surface mesh.

Characterization of Surfaces

It should be possible to characterize the surface of a solid in essentially the same way as any other interacting assemblage of atoms such as a molecule or a bulk solid. We must specify: (i) the chemical identity of the atoms present; (ii) the geometrical or structural arrangement of these atoms; and (iii) the energy level structure of their outermost or valence electrons. Such characterizations of the static surface will be important in understanding the dynamic interactions of surfaces with external interactants such as photons, atoms, and molecules. In fact, the dynamic interactions and the static characterizations of a surface are inextricably intertwined since tools are devised from the former to determine the latter.

The principal means for the chemical identification of surface atoms now in use is the so-called Auger electron spectroscopy (AES) (*2*). With this method the investigator makes use of the fact that electrons ejected from surface atoms as they relax after ionization of a core electron have characteristic energies dependent on core level energies and thus on chemical identity. It is quite easy to determine the symmetry of surface structures such as those depicted in Fig. 2 from the symmetry of diffracted electron beams observed by the method of low-energy electron diffraction (LEED) (*3*). Determination of specific atom positions is much more difficult and depends on a detailed understanding, which we are now acquiring, of the variation of the intensity of diffracted electron beams on the energy or wavelength of the incident electrons. The means by which the surface energy level structure is being determined, the third basic characterization of a solid surface, is the subject of this article. There are three experimental methods in current use which will be discussed below.

Significance of Electron Energy Level Spectra

All interactions of a surface with its surroundings are, in part at least, electronic interactions whose characteristics must certainly depend upon the distribution in energy of electronic states in the surface monolayer. Thus, for example, chemical reactions at surfaces, which involve electron sharing and possibly electron exchange, should differ in character and kinetics among surfaces whose electron energy level structures differ.

A knowledge of the electron energy level structure is also important because of its relations to atomic structures and chemical identity, the other two surface characterizations. As an example let us consider a surface to which foreign atoms are chemisorbed in an ordered array. Chemisorption implies strong interaction of the adsorbate with one or more surface atoms of the adsorbant. We may thus be dealing with a situation in which the interactions among the atoms involved in this bonding, the so-called surface molecule or surface complex, are as strong as or stronger than the interaction of this structure with the substrate. The energy states of such a surface molecule, even though they are shifted and broadened by the interaction of the surface molecule with the underlying solid, will, as for free molecules, be intimately related to the symmetry and structure of the local atomic arrangement.

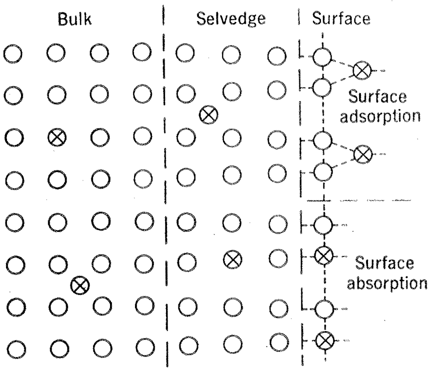


Fig. 1. Schematic view of a planar cut into a crystalline solid showing surface, selvedge, and bulk: lattice atoms, open circles; foreign atoms, crossed circles.

Nature of Surface Energy Levels

The sharp energy levels of atoms are spread out into energy bands in a solid because of the interaction among electrons of neighboring atoms. Since surface atoms have fewer neighbors than bulk atoms, the surface energy level spectrum will be less solid-like and more atom-like than the bulk spectrum. This effect is particularly strong for bands which, by virtue of weak overlap of wave functions, have a narrow energy spread in the bulk. Thus the *d*-bands of a transition metal should be narrower at the surface than they are in the bulk because of the reduced number of nearest-neighbor atoms. For the surface of any solid an appropriate designation of a surface energy level spectrum is the density of electronic energy levels weighted by the magnitude of the wave function at the surface. This has been called the local density of states at the surface and is a modification of a similar localized function definable for the bulk solid.

When foreign atoms are adsorbed at, or absorbed into, the surface monolayer, we may employ the concept of a resonance or a virtual bound state to describe the electronic energy level structure (*4, 5*). Consider, for example, a chalcogen atom such as oxygen, sulfur, or selenium which has four *p* electrons in a single degenerate energy level when the atom is free, a large distance from the solid surface. When the chalcogen atom is brought up to the surface and is chemisorbed to it, the discrete atomic *p* level interacts with the solid, broadens, and shifts to a different energy (*5*). If the four *p* electrons of the chalcogen go into inequivalent orbitals at the surface, the single degenerate atomic level is replaced at the surface by several broadened levels. Strictly speaking, these are no longer energy levels associated with the chalcogen atom. They are now called resonances and are characteristic of the whole metal-atom system with many electronic states participating in them.

A resonance is an interval on the energy scale in which at the position of the adsorbed atom the amplitude of the electronic wave function is enhanced over what it would be at this point in space and at this energy in the absence of the absorbed atom. It is a particularly appropriate concept in terms of which to discuss the energy level structure at a surface. Although it is introduced here for the case of adsorbed atoms which are chemically different from substrate atoms, the concept may also be used for atomically clean surfaces. In this case, for example, the surface *d* levels of a transition element may be looked upon as *d* resonances of the surface atom on its own substrate. In the case of chemisorption the electrons in each inequivalent chemical bond will produce a resonance at a distinct energy. These resonances will appear on a background of energy levels appropriate to the underlying solid.

Surface Energy Level Spectroscopies

Any experiment designed to yield information about a surface must, to a degree, be specific to the surface. The ideal electronic spectroscopy of the surface monolayer would be sensitive to the surface alone and would ignore electrons resident in the selvedge or bulk solid beneath. Clearly no such ideal spectroscopy exists; thus it is advantageous to use several methods of differing surface specificity.

The type of spectroscopy expected to be most useful in determining surface energy level structure is an electron spectroscopy in which electrons are ejected from the solid by an electron emission process. This type of spectroscopy is useful for two reasons. One reason is that the energy of the emitted electron determines the final state energy of the transition by means of which the electron was excited. This feature may not be shared by spectroscopies based solely on the absorption or emission of radiation, since in many cases we know only that a transition has occurred between two levels of the proper separation without knowing the absolute energy level of either. The other reason is the enhancement of surface specificity which results from the strong electron-electron interaction which limits, in some cases, the mean free path of unscattered electrons to at most a few monolayers. Three electron spectroscopies which have been applied to surfaces are illustrated by the energy level diagrams in Fig. 3. Each is based on an electron emission process, and in each the spectroscopic information is contained, in one form or another, in the kinetic energy distribution of these ejected electrons.

Figure 3A depicts an energy level diagram characterizing field-emission spectroscopy (FES) (*6*). Here the solid is provided in the form of a sharp point at which it is possible by the application of voltage to produce a strong surface electric field. This field is of such sign as to produce a peaked potential barrier at the surface through which electrons from the filled band of the solid can tunnel into the vacuum outside. One measures the relative numbers of such field-emitted electrons of variable energy E above the vacuum energy level at a large distance from the point. Field-emission spectroscopy has the very great advantage that it is very surface-selective. All observed electrons must tunnel through the surface. Surface electronic resonances have been shown to have a strong effect upon the tunneling probability as a function of energy. The method has been perfected and is being used in very interesting studies of adsorbed atoms on surfaces. However, the method does have distinct disadvantages. Its principal disadvantage is that it is possible to explore an energy range extending only 2 to 3 electron volts below the Fermi level in metals or below the top of the filled valence band in semi-

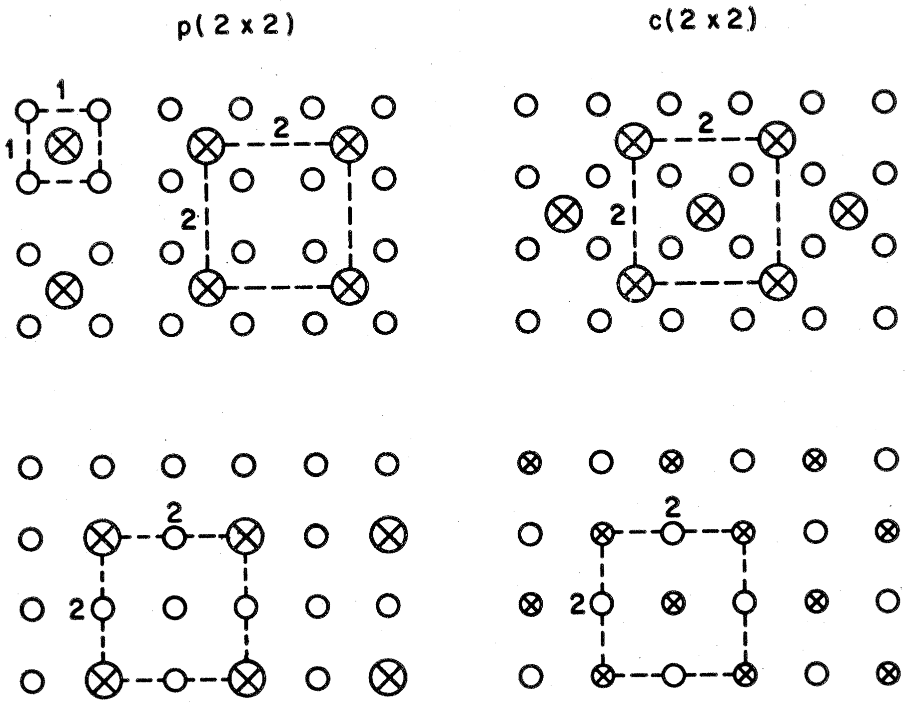


Fig. 2. Face-on schematic view of the (100) surface of a cubic crystal showing possible adsorbed or absorbed surface structures involving foreign atoms.

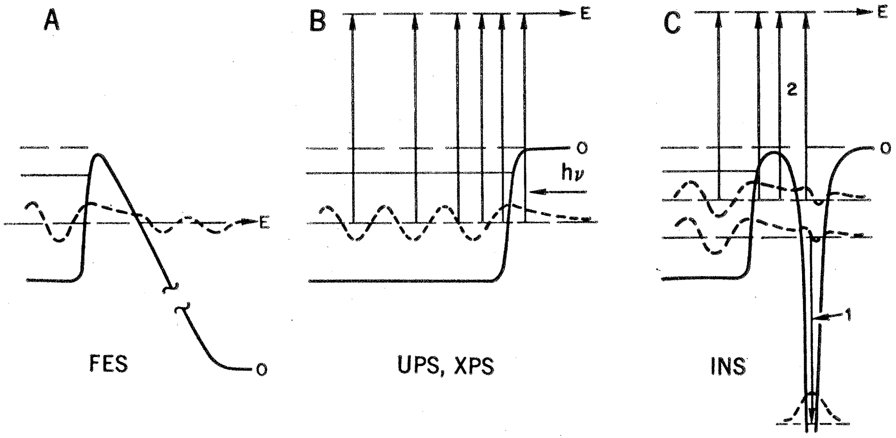


Fig. 3. Energy level diagrams depicting three electron spectroscopies applied to the determination of energy level structure at solid surfaces: (A) FES; (B) UPS, XPS; and (C) INS. The dashed lines indicate wave functions of electrons in various states. The vertical arrows in (B) and (C) are meant to suggest that electron excitation can occur at various distances into the solid.

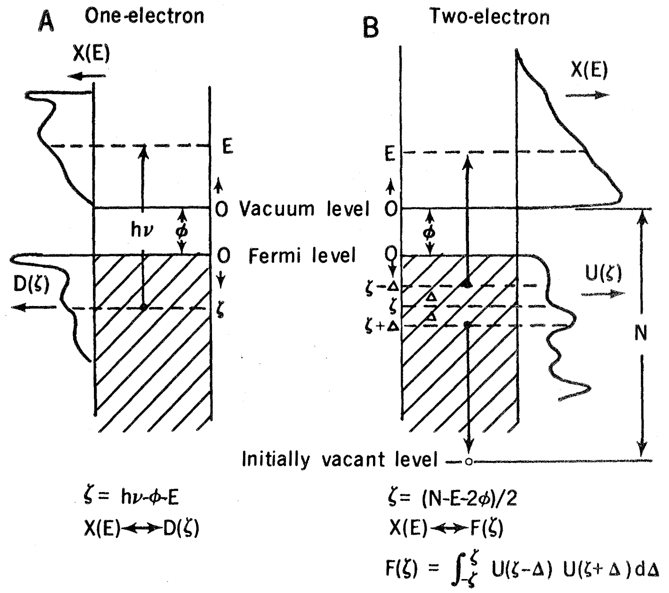


Fig. 4. Energy level diagrams of (A) the one-electron photoemission process and (B) the two-electron ion-neutralization process. Electron energy distribution functions are shown in each case. The single electron in (A) is excited by an amount of energy *hν*, the energy of the photon absorbed. The up and down transitions of the two electrons in (B) are of equal magnitude.

conductors. Furthermore, the local density of states must be extracted from an emission current function which varies by a factor of 10^7 over an energy range of 2 ev. The experimental difficulties involved in forming the sharp emitter point and in measuring the energy of kiloelectron-volt electrons with the required resolution are well in hand. However, the large field required at the surface could cause field desorption in some cases, thus making it impossible to study some surface structures by FES.

In Fig. 3B the photoemission process is depicted (*7*). A photon is absorbed by an electron in the solid and is thereby excited to the energy level *E*. The excited electron may leave the solid without loss of energy if it is produced sufficiently close to the surface of the solid. If the photon is in the ultraviolet frequency range the spectroscopy is called ultraviolet photoelectron spectroscopy (UPS); if in the x-ray range, x-ray photoelectron spectroscopy (XPS). In each case the kinetic energy distribution of ejected electrons is measured. With XPS it is possible to explore energy levels of core electrons of atoms in addition to the higher-lying valence states (*8*).

Among the spectroscopies depicted in Fig. 3 it is quite clear that the photoemission methods have singular advantages. These include the relative ease of application and the possibility of excitation from states lying in a wide energy range. It has recently been demonstrated that UPS can definitely be applied to the study of surfaces in two important ways. In one piece of work it has been shown that electrons in orbitals in the carbon monoxide molecule and in the oxygen atom when sorbed at a nickel surface can be observed by UPS (*9*). Another example is the determination of the density in energy space of electrons in a surface state on Si(111) which overlaps the top of the bulk valence band (*10*). These are exciting developments and presage an important role for UPS in surface physics. Because of the nature of the photoemission process it will be necessary, however, to learn much more than we now know about the relative roles of bulk and surface effects in UPS.

I shall discuss later in this article one way in which information on this point may be obtained by comparing the results of different electron spectroscopies [ion-neutralization spectroscopy (INS) and UPS] having differing degrees of surface specificity.

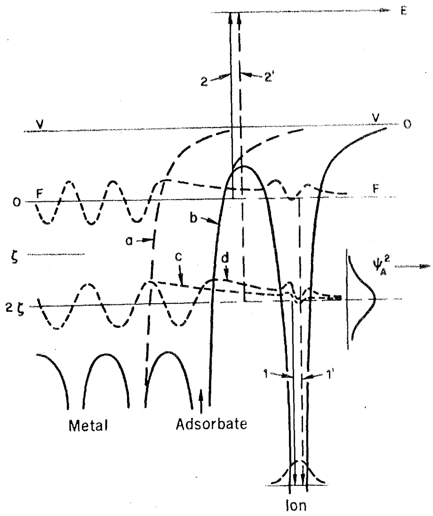


Fig. 5. Energy level diagram illustrating why INS is particularly sensitive to the presence of surface resonances.

Other ways of disentangling photoexcitations occurring in the bulk and selvedge are the variation of the angle of incidence of unpolarized light (see below) or the rotation of the plane of polarization of polarized light at oblique incidence.

The third electron spectroscopy based on an electron transition process is INS (*11*) (Fig. 3C), with which I am principally concerned in this article. Unlike FES, UPS, and XPS, INS is based on an electronic transition process in which two electrons participate. The process occurs when a slowly moving, singly charged, positive ion presented just outside the solid surface is neutralized to the ground state of the parent atom. The sole reason for bringing the ion up to the surface is to provide a vacant low-lying level to initiate the two electronic transitions. One electron from the solid tunnels through the barrier between surface and ion and drops into the ground atomic state. In a radiationless process of an Auger type a second electron accepts the energy released in the downward transition of the first electron. This second electron is thereby exicted to the energy *E* and may leave the solid if properly directed. Its kinetic energy distribution is measured.

Ion-Neutralization Spectroscopy

The development of INS grew out of studies of the interesting families of electron transition processes which can occur between atomic particles and solids when slow ions, excited atoms, or excited ions are brought near a solid surface (*12*). These studies clearly demonstrated the sensitivity to surface conditions of the energy distributions of electrons ejected from the solid in the ion-neutralization process. This led to the attempt to develop a viable spectroscopy based on this two-electron process (*5, 11*). It is not much more difficult to provide a slow ion beam of large neutralization energy than a beam of high-energy photons with the use of a resonance lamp. However, the two-electron character of the Auger-type process upon which INS is based causes the measured kinetic energy distribution to be related to the integral self-convolution of the local density-of-states function we are seeking. As I will show later, it is this feature which complicates the data-reduction procedures of INS.

Ion-neutralization spectroscopy possesses one feature shared by FES but not by UPS or XPS. It is that the neutralizing electron must tunnel through the surface into the approaching ion. For this reason INS is very surface-selective, like FES, and this feature is the principal justification for the effort expended in its development. Also there is good evidence that those excited electrons in INS which leave the solid originate outside of or in the surface region of the solid and hence do not interact with the solid nearly as much as photoemitted electrons.

Contrast of INS and UPS

The basic features of UPS as a one-electron spectroscopy and INS as a two-electron spectroscopy are contrasted in Fig. 4. In the one-electron spectroscopy (Fig. 4A) there is a one-

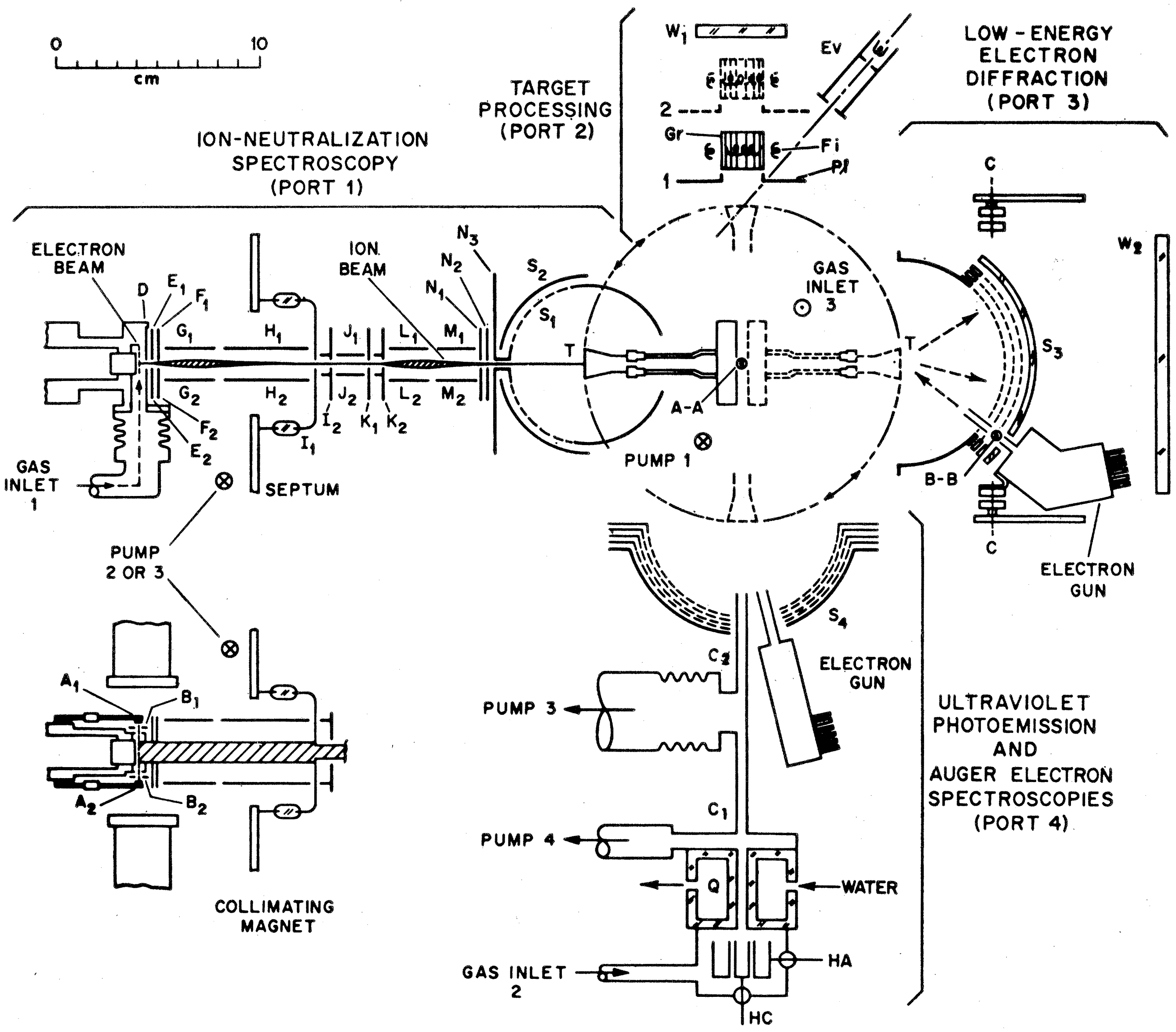


Fig. 6. Schematic diagram of an experimental apparatus with which it is possible to perform several surface experiments on the same crystal in the same vacuum environment. This view is a slightly modified top view of the apparatus attached to the four horizontal ports of the six-ported vacuum enclosure. The single-crystal sample or target *T* can be turned around axis *A–A* so as to be incorporated into any one of the experiments included at ports 1 to 4. In the diagram of the INS apparatus at port 1 a side view is shown instead of a top view from electrode *D* to electrode N_3 because it is more informative. A top view of the ion source region is shown below. An electron beam emitted from filament A_1 or A_2 is accelerated through a slit in electrode B_1 or B_2 into the ionization chamber *D*. Ions formed from helium or neon gas in *D* are drawn out through electrodes $E_{1,2}$ and $F_{1,2}$. The ion beam is focused by electrostatic lenses formed by the *G, H* electrodes, the *L, M* electrodes, and electrodes $N_{1,2,3}$. Apertures in I_1, K_1, and K_2 also collimate the ion beam. The ion beam may be deflected in directions perpendicular to its axis by cross voltages applicable between any symmetrical pair of electrodes having the same letter designation but the different subscripts 1 and 2. The energies of electrons ejected from *T* in the ion-neutralization process are analyzed by the degree of retardation between the grid S_1 and the hemisphere S_2. In the target-processing port (port 2) *Fi*, *Gr*, and *Pl* are, respectively, the electron-emitting filaments, the grid, and an apertured plate for use in sputtering the sample to clean it. Ions formed inside the grid cage *Gr* from neon or argon gas are pulled through the aperture in *Pl* to the target *T*; *Ev* is an evaporator for coating the sample with evaporable material, and W_1 is a viewing window. In the LEED port (port 3) S_3 is a phosphor-coated spherical glass screen with the usual three-grid deceleration-acceleration system in front of it. The electron beam can be scanned over the target face by moving the electron gun on gimbals whose axes are *B–B* and *C–C*; W_2 is the viewing window. At port 4 a four-grid electron-retardation analyzer is used for both UPS and AES. The light photons for UPS are generated in a water-cooled quartz capillary lamp *Q*; *HA* and *HC* are annular and cylindrical hollow cathodes, respectively, and C_1 and C_2 are differentially pumped vacuum-isolation capillaries through which the light reaches *T*. The electron gun provides 3000-ev electrons for the AES experiment.

to-one correspondence between the initial state of the participating electron at the energy ζ below the Fermi level and the final state after excitation to the energy E above the vacuum level V. The measured kinetic energy distribution, $X(E)$, of the ejected electrons may not reflect directly the density of initial states since in photoemission it can depend upon the joint density of states as well as transition probability factors.

In INS, on the other hand, as Fig. 4B shows, the final state E of an excited electron corresponds to an infinite set of initial states. These are the pairs of states symmetrically disposed, each at an energy separation Δ, with respect to that energy level at ζ lying halfway between the energy E and the ground level of the parent atom which is initially vacant in the ion. This basic characteristic of the two-electron process means that $X(E)$ is related to a function $F(\zeta)$, the integral self-convolution of the function $U(\zeta)$ that contains the spectroscopic information we desire. Thus after extrapolation of $X(E)$ to remove energy-broadening, it is necessary to deconvolve or unfold the result to obtain $U(\zeta)$. This is done readily by a sequential procedure on a digital computer with the use of the $X(E)$ data obtained in digital form in the experiment.

The nature of the surface selectivity of INS upon which its sensitivity to surface resonances is based is illustrated in Fig. 5. Here the monolayer adsorbate may be thought to extend the surface barrier of the metal substrate from *a* to *b*. The adsorbate produces a resonance over a limited energy range as indicated by the square of the wave function, $\Psi_A{}^2$, plotted at the right in Fig. 5. In the energy range of the resonance, electron wave functions, *d*, tunnel readily through the adsorbate monolayer. The function *c* indicates how the wave function would look in the absence of the adsorbate. It resembles the function shown at the Fermi level *F* which lies outside the energy range of the adsorbate resonance and is thus essentially unaffected by the presence of the adsorbate. This diagram illustrates how the magnitude of the wave function at the position of the ion is enhanced for electrons in the energy range of the resonance, thus increasing the probability of their involvement in the ion-neutralization process.

The necessity to unfold the data in INS has led us into an interesting and instructive study of the interrelated roles played by physics and mathematics in the proper solution of the problem (*13*). Deconvolution or unfolding involves the solution of an integral equation which cannot be obtained in the general case. However, the physical nature of the process we are studying limits us to a class of mathematical functions for which not only a solution but also a mathematical test of the correctness of the solution is possible. Thus we now possess both the knowledge and the mathematical means to handle the data correctly. The effort required in data reduction in INS, as compared to that required in UPS, for example, is justified for surface studies in terms of the greater surface selectivity of INS. Some of these comparative studies will be mentioned after a discussion of the experimental apparatus with which they have been carried out.

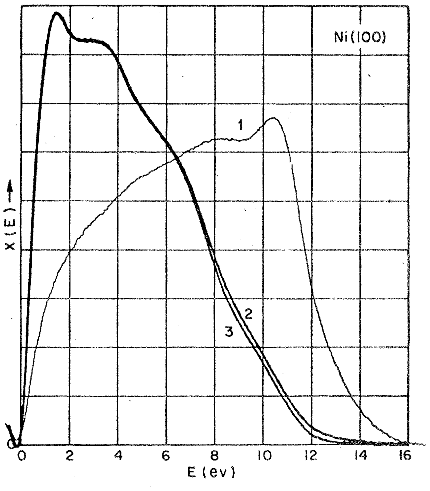


Fig. 7. Kinetic energy distributions obtained by the use of He$^+$ ions in INS. Curve 1 is for 10-ev ions on a clean Ni(100) surface. Curves 2 and 3 are for 20- and 10-ev ions, respectively, on the Ni(100)c(2$\times$2)Se surface. Two $X(E)$ curves for different ion energies such as curves 2 and 3 are used to obtain an extrapolated curve having little energy-broadening which then forms the basis of the data reduction to determine the $F(\zeta)$ and $U(\zeta)$ functions of Fig. 4B.

Versatile Apparatus for Surface Studies

A schematic diagram of the apparatus with which surfaces may be studied in a variety of ways is shown in Fig. 6. The vacuum chamber consists of a three-dimensional cross of stainless steel tubing with an inner diameter of about 17 centimeters terminating in vacuum flanges. This arrangement provides six ports into the vacuum chamber of the apparatus. The four ports in a horizontal plane, to which are bolted the apparatus required for the various experiments, are shown schematically in Fig. 6. To port 1 is attached the INS apparatus; to port 2, apparatus for sample-processing; to port 3, the LEED apparatus; and to port 4, apparatus for both UPS and AES. Of the two remaining ports the top port carries a sample-turning mechanism, not shown in Fig. 6, which can present the single crystal sample to any one of the horizontal ports as is seen in Fig. 6. The bottom port connects the chamber to the vacuum pumps and gas supply.

A brief statement of the modus operandi of each experiment follows. At port 1 a focused, slow ion beam is provided for INS studies. The energies of the electrons ejected from the single-crystal target *T* are analyzed by retarding fields between the grid S_1 and the spherical collector S_2. The ion beam is generated by electron impact within electrode *D* and is focused and collimated by the series of lenses and apertures provided by electrodes *E* through *N*. At port 2 the target-processing which can be performed includes heating, sputtering, and exposure to gases or beams of evaporated material. At port 3 LEED measurements can be used to determine the crystallography of the surface under study. A windowless capillary discharge source of resonance radiation for UPS is provided at port 4. It may be used to generate both the atomic (He I, 21.2 ev; Ne I, 16.8 ev) and ionic (He II, 40.8 ev; Ne II, 26.9 ev) resonance lines. An electron gun which produces an electron beam (3 kiloelectron volts) for AES is also provided at port 4. The energies of electrons ejected from the target in either of these spectroscopies are analyzed by the grid system and collected at S_4.

A historical note may interest the reader. The basic apparatus including ports 1, 2, and 3 was designed about a decade ago and has been used for a variety of INS and particle-solid interaction studies in the intervening years (*5, 11*). Port 4 was designed, built, and tested during the last 2 years or so. Although a multiplicity of experiments adds considerably to the rigors of experimentation, it also provides a very important ingredient for basic surface work, namely, the capability of "looking" at the same surface with many "eyes." The importance of this kind of experimentation in surface research at the present time can hardly be overemphasized. It is clear that the newly expanded apparatus is designed to yield, for a given surface, data on each of the surface characterizations discussed earlier. Whereas comparisons of INS and LEED have been possible for many years, we are at the threshold of intercomparing INS, UPS, AES, and LEED.

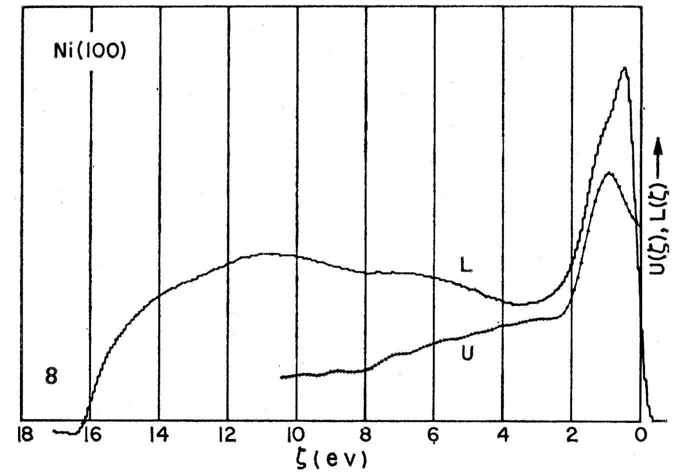
Some Results Obtained with INS

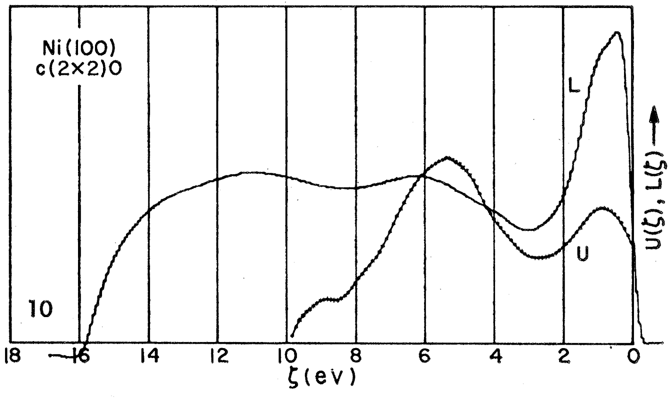
Examples of basic data obtained by INS are shown in Fig. 7. These are kinetic energy distributions of electrons ejected by 10-ev He^+ ions from atomically clean Ni(100) (curve 1) and by 10- and 20-ev He^+ ions (curves 3 and 2, respectively) from a Ni(100) surface with a c(2 × 2) structure of selenium atoms adsorbed upon it. Each of curves 2 and 3 consists of five XY-recorder traces superposed. When digital data corresponding to curve 1 are processed, they yield the $U(\zeta)$ function of Fig. 8. Curves 2 and 3 yield the $U(\zeta)$ function shown in Fig. 9. The $U(\zeta)$ function represents the density in energy space of transitions of the ion-neutralization process. It depends, like the analagous function obtained from any electron spectroscopy, upon transition probability and local state density factors. The U curve for clean Ni(100) (Fig. 8) shows a narrow *d*-band of the surface nickel atoms lying just below the Fermi level ($\zeta = 0$). The U curve for Ni(100)c(2 × 2)Se of Fig. 9 shows several peaks due to resonances of electrons in the surface selenium structure. The U function in each case resembles the differential of the $X(E)$ function. This is a characteristic of the deconvolution for the general class of mathematical functions with which we must deal (*13*).

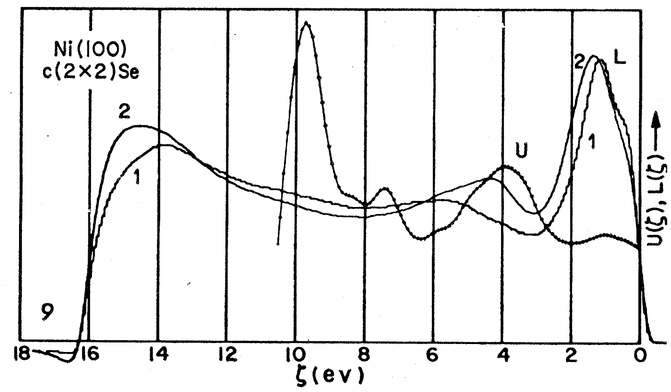
A principal goal in the use of INS to date has been the study and understanding of a series of related surfaces produced by chemically similar adsorbates on several crystal faces of the same solid. In this way it has been possible to build systematics concerning these surfaces which have made more complete understanding possible. The principal effort of this kind has been the study of oxygen, sulfur, and selenium on the (100), (110), and (111) faces of nickel (*5, 14*). This work has demonstrated the viability of INS as a detector of surface resonances and has shown that different orbital spectra are obtained when similar atoms are adsorbed in different repeat arrays on different crystal faces. It also demonstrates how the shift in energy of a surface orbital from the energy of the parent atomic orbital can be combined with the change in the work function on adsorption to yield information about charge shifts and bonding structure. Another exciting experimental result, observed in a study of sulfur and selenium on Ni(100), is the change in the orbital energy spectrum accompanying the change in surface repeat pattern from c(2 × 2) to p(2 × 2). Thus the molecular structure in the local bonding site is sensitive to the specific surface crystallography. Since these experiments are reported extensively elsewhere (*5, 14*), I shall conclude this article by discussing briefly some recent work aimed at comparing INS and UPS.

Direct Comparison of INS and UPS

With the apparatus shown in Fig. 6 it is possible to compare INS and UPS directly and to shift rapidly from one







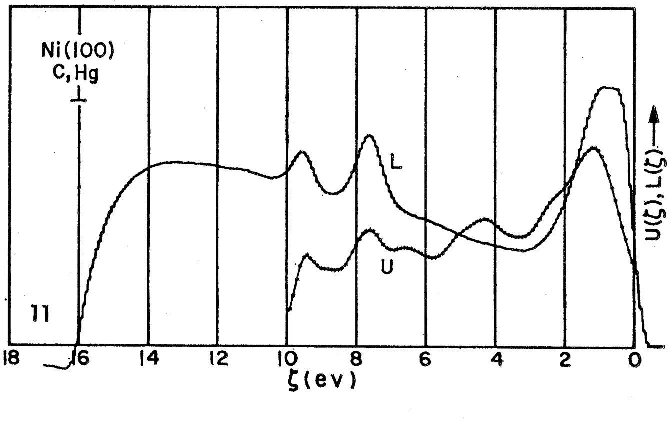


Fig. 8 (upper left). The $U(\zeta)$ and $L(\zeta)$ functions from INS and UPS, respectively, for atomically clean Ni(100). Fig. 9 (lower left). The $U(\zeta)$ and $L(\zeta)$ functions for the Ni(100)c(2×2)Se surface. Curve 1 is the $L(\zeta)$ function for light of normal incidence; curve 2 is for light with an angle of incidence of 45°. Fig. 10 (upper right). The $U(\zeta)$ and $L(\zeta)$ functions for the Ni(100)c(2 × 2)O surface. Fig. 11 (lower right). The $U(\zeta)$ and $L(\zeta)$ functions for a Ni(100) surface at which both carbon and mercury atoms are sorbed.

method to the other. We see in Fig. 8 that, for clean Ni(100), INS with He^+ ions and UPS with normal-incidence 21.2-ev He I radiation yield quite similar results. The $L(\zeta)$ function plotted here is the $X(E)$ function of Fig. 4A, after the variable change from E to ζ appropriate to the photoemission process has been made. Similarly, when a $c(2 \times 2)O$ structure involving oxygen is formed on Ni(100), both methods indicate the presence of a broad oxygen orbital centered at $\zeta \sim 5.5$ ev (Fig. 10) (*9*). In view of this agreement, one may be tempted to conclude that the two methods are responding with differing sensitivities to the same surface feature. Although this is certainly true in part, it is not the whole story as is demonstrated by the results of the following experiment. The Ni(100)-$c(2 \times 2)O$ surface was heated to successively higher temperatures. After each heating both INS and UPS measurements were made. The UPS $L(\zeta)$ curve was found to remain essentially invariant in the range of the oxygen resonance. Heating, on the other hand, caused the INS distribution to revert toward that characteristic of the clean Ni(100) surface. A probable explanation of these results is that the heating caused the surface oxygen to move into the bulk, reducing the surface concentration to which INS is more sensitive than UPS but not changing the oxygen concentration in the selvedge in that depth from which photoelectrons are extracted. What the similarity of the UPS and INS results in Fig. 10 is really telling us, therefore, is not that the same orbital is being observed but that the orbitals of oxygen in the bulk and of surface oxygen are very similar. This result is not so farfetched if it is in fact true that the surface oxygen is absorbed into the surface monolayer as concluded earlier (*5*) and not adsorbed to it.

Another comparison of UPS and INS results is shown in Fig. 11. Here the light and ion beams are incident normally on a nickel surface which has both carbon and mercury on it. The resonance peaks in $L(\zeta)$ at 7.8 and 9.7 ev are due to electrons which are ejected, respectively, from the $5d_{5/2}$ and $5d_{3/2}$ levels of the mercury atom. The orbital clearly seen in the INS $U(\zeta)$ curve at $\zeta = 4.2$ ev is not present in the $L(\zeta)$ curve. In a different experiment at 45° incidence with only mercury on the surface the same orbitals at 7.8 and 9.7 ev are also seen.

A third comparison between UPS and INS results is that for the Ni(100)-$c(2 \times 2)Se$ surface shown in Fig. 9. This surface has been studied at both normal and oblique angles of incidence. The U curve of Fig. 9 was taken at normal incidence but its essentials do not change with incidence angle. Note the differences between the kinetic energy distribution, L_1, of photoejected electrons at normal incidence and that, L_2, taken at oblique incidence. Whereas none of the orbital peaks seen in the U curve are to be found in curve 1 of the two L curves, curve 2 does show one broad peak with maximum near $\zeta = 4$ ev. Here we see the effect of the angle of light incidence on our ability to detect surface resonances as well as another striking example of the differences between UPS and INS as surface probes.

I shall briefly recapitulate the results to date of comparing INS and UPS. Electrons in some surface orbitals, the d levels of mercury, for example, may be observed with INS and UPS at both normal and oblique light incidence. Electrons in the orbitals derived from the p^4 electrons of selenium when chemisorbed to nickel may be observed by INS, not observed by normal incidence UPS, and partially observed by oblique-incidence UPS. And finally, oxygen sorbed to Ni(100) is seen to yield similar orbital peaks by UPS and INS but there is subsidiary evidence which can be interpreted to mean that the electrons observed by the two methods are connected with atoms in different regions of the crystal. All of these facts will have to be understood in terms of the specific characteristics of the electron-ejection processes upon which UPS and INS are based. Orbitals seen by INS are those which have the strongest effect on the magnitude of the electronic wave function projecting from the surface toward the incident ion as it approaches the surface. Orbitals seen best by UPS are those lying in regions of the crystal where the electrostatic potential has the largest gradient along the direction of the electric field vector of the incident light, provided they are not excluded by an optical selection rule (*15*).

Conclusions

At this point it would be presumptuous to suggest either that we understand very much about the electronic structure of solid surfaces or that we can specify in detail exactly what each of our tools for studying such structure is telling us. I think it is fair to say, however, that FES, UPS, and INS do make it possible for us to determine energy level spectra which can with some confidence be ascribed to the resonances of electrons in surface orbitals. It is true that INS is the more surface-selective of the two electron spectroscopies capable of producing data over at least a 10-ev energy range. We have seen intriguing differences between INS and UPS which, when we come to understand them, will most certainly reveal important characteristics of surface electronic structure and greatly expand our ability to distinguish electronic states in the surface from those in the selvedge. Possibly it is not too much to hope that the combined use of INS and UPS with incidence angle as an independent variable will give us information on the geometrical extent of surface orbitals, as well as the net electrical charge and the electric potential gradient in the region of the surface in which the orbitals lie.

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