SURFACE PHYSICS

Inner-shell spectroscopy

Many methods are available whereby transitions involving core electrons reveal the identities of atoms in the surface region and their local electronic environments.

Robert L. Park

If a surface exposed by cleaving a mica sheet is sprayed immediately with distilled water from an atomizer, the water seems to disappear as it uniformly wets the surface. If several seconds had been allowed to pass before the surface were sprayed, the water would bead up in distinctly visible droplets. In that brief moment the surface has been contaminated by organic vapors from the laboratory air; even at a pressure of 10^{-12} atmospheres, a complete monolayer of contamination can condense on a surface in less than an hour. Such layers may determine the characteristics of the surface with respect to lubrication, corrosion, catalysis, emissive properties and adhesion; yet prior to 1967 no general method existed by which the surface composition could be analyzed.

Today, a bewildering array of spectroscopies are used to examine the elemental composition of solid surfaces. I will deal here with six types that involve the inner (core-level) shells of the surface atoms. The first three examples, Auger electron, soft x-ray emission and ion-induced x-ray spectroscopies monitor recombination phenomena—the coming together of an outer electron and a previously vacated inner "hole." The other three examples, appearance potential, x-ray photoelectron and core-level characteristic-loss spectroscopies, examine the creation of the inner hole by the excitation of core electrons to states above the Fermi level. Although these spectroscopies were developed by basic researchers facing research problems that could not be addressed by existing techniques, they are used routinely in such applied areas as microcircuit technology.

Indeed, the tools of applied technology frequently owe their origins to the demands of basic research. The core-level surface spectroscopies, though, remain of interest to the basic researcher not only because the factors that determine surface composition remain obscure, but because of the unique view they provide of surface electronic structure.

The surface region of a solid might reasonably be defined as the layer in which the atomic potentials differ from those of atoms still deeper within the solid. This layer includes adsorbed foreign atoms, but it also includes those substrate atoms that sense the loss of translational symmetry. For clean metals the surface region may include no more than the outermost two atomic layers. The composition in this region can be inferred either from the energies required to create vacancies in the inner electronic shells (which are nearly unaffected by the chemical environment) or from the energies of the electronic transitions involved in the decay of the vacancies. We will see that the extent to which such measurements are specific to the surface region depends on the mean free path for inelastic scattering of electrons.

Both the excitation and recombination transitions may involve states within a few electron volts of the Fermi energy. The line shapes associated with these transitions should thus reflect the chemical environment of the atoms. The view is, however, very different from that provided by techniques such as ultraviolet photoelectron spectroscopy described in this issue by Dean Eastman and Marshall Nathan or the vacuum-tunneling spectroscopies described by E. Ward Plummer, David Penn and John Gadzuk, which respond to a state density averaged over all surface species. Core-level transitions by contrast are specific to a *single* element. It therefore should be possible to examine separately the local density of states associated with different elements on the same surface by using the core levels as windows (see figure 1). The price paid for this localized view is that the features are smeared out by the uncertainty in the core-electron binding energy. This uncertainty is a consequence of the finite lifetime of a core hole.

Auger electron spectroscopy

In principle, any incident particle of energy greater than the binding energy of an inner-shell electron can excite that electron into an unoccupied state above the Fermi level. The core vacancy left behind will be filled by an electron from a higher level as the atom, in a series of transitions, convulses its way back to the ground state. This reorganization is generally independent of the mode of excitation, because the decay time is long compared to the excitation time. The decay time is, however, sufficiently finite as to produce a measurable uncertainty in the energy of the deep level. Energy is conserved in the decay transitions by the emission of x-ray photons or Auger electrons as shown in figure 1. In the energy range of interest for surface studies (less than 2 keV) Auger transitions are heavily favored.

Auger electrons were first identified in secondary-electron energy distributions of electron bombarded surfaces by James Lander in 1953,[1] but only the

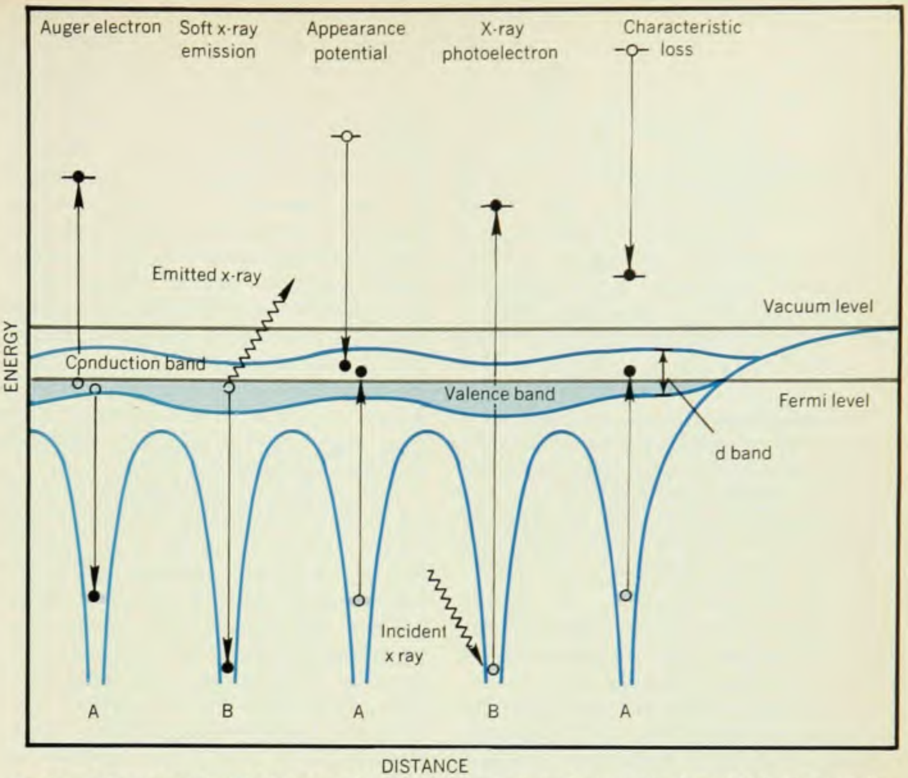
---

Robert Park is professor of physics and director of the Center of Materials Research, University of Maryland, College Park.

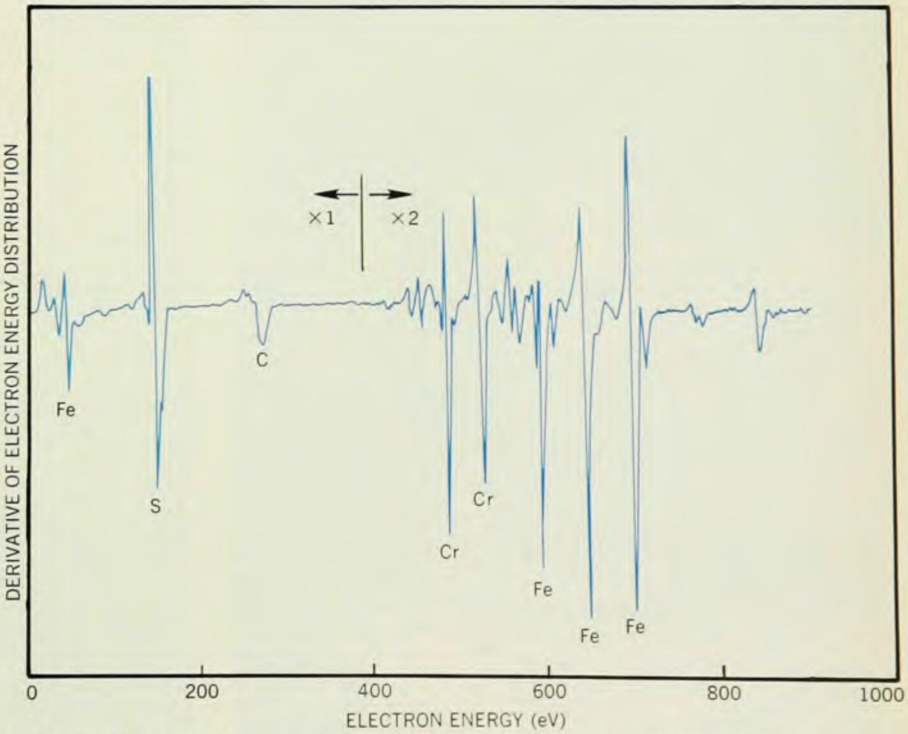
most intense Auger transitions could be detected in the hail of secondary electrons resulting from the strong interaction of the incident electron beam with the valence electron fluid of the solid. Electron-excited Auger electron spectroscopy thus did not appear to offer a sensitive method of surface analysis. Fifteen years later, however, Lawrence Harris[2] demonstrated that by simply taking the derivative of the secondary emission spectrum, the Auger emission features could be greatly enhanced (figure 2). Harris was exploiting the fact that Auger features are distinguished from most of the remainder of the spectrum by their relative sharpness. Every spectroscopy relies on some such distinguishing characteristic to sift the desired signal from a background of unwanted emissions. Differentiation has become an important means of extracting discrete spectra from continuous backgrounds and we will encounter it again in the discussion of other core-level spectroscopies.

The impact of Auger electron spectroscopy on the field of surface physics is difficult to overstate. Prior to its development, every surface experiment was subject to the criticism that surface cleanliness could not be characterized. The acceptance of Auger spectroscopy was made easier because many surface physicists already had spherical grid low-energy electron diffraction systems, described by Peder Estrup in this issue, which could be converted to retarding-potential energy analyzers by the addition of external electronics.[4] Because of the obvious advantages of coupling LEED with Auger spectroscopy, the retarding analyzer remains an important instrument. For applications where LEED would be irrelevant, there is wide use of electrostatic deflection analyzers, which permits the spectrum to be scanned in a relatively short period of time.

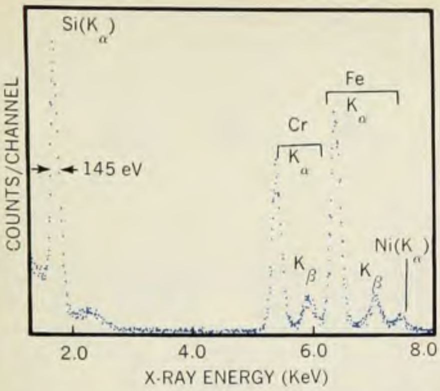
The acquisition of the spectrum may, however, be far simpler than its interpretation. The complexity results from the fact that an Auger line represents term differences between three levels. For example, a transition labelled KL_1L_2 refers to an initial vacancy in the K shell (1s) that undergoes a transition to holes in the L_1 (2s) and L_2 ($2p_{1/2}$) shells plus an Auger electron. For a heavy element the L-shell Auger spectrum alone consists of hundreds of lines, the energies of which are not susceptible to precise first-principle calculations. It is generally possible to identify spectral groups, but not individual features within those groups. Serious ambiguities therefore arise in the identification of Auger transitions for all but the lightest elements, and elemental analysis is generally based on matching spectra against "standard" plots taken from samples of known composition.



A schematic energy-level diagram of a hypothetical alloy of elements A and B (with partially filled d bands) serves to show the differences in various core-level spectroscopies. For the two recombination types—Auger electron and soft x-ray emission—energy is conserved after a valence electron recombines with a core vacancy when either an Auger electron or a characteristic x ray is emitted. Core-level binding energies are determined in appearance-potential spectroscopy from the least energy that can excite a core hole. In photoelectron spectroscopy the surface absorbs photons of known energy; the energies of ejected photoelectrons are then measured. Characteristic-loss spectra are obtained by determining the minimum energy given up by an incident electron in creating a core hole. The core-level transitons allow the local electronic environment of elements A and B to be examined separately. Figure 1



Auger emission lines become distinct when the derivative of the secondary-emission energy distribution is taken. This spectrum, taken by Paul Palmberg of Physical Electronics Industries, is of a stainless-steel surface bombarded with 5-keV electrons. Elemental identification is generally done by matching spectra against "standard" plots from samples of known composition. Note the change in scale near 400 eV. Taken from reference 3. Figure 2



This proton-induced x-ray spectrum of a stainless-steel surface resulted from bombarding the surface with 350-keV protons. Detector resolution is about 145 eV. Such spectra provide information on elemental abundance, but no information on electronic structure. From reference 12. Figure 3

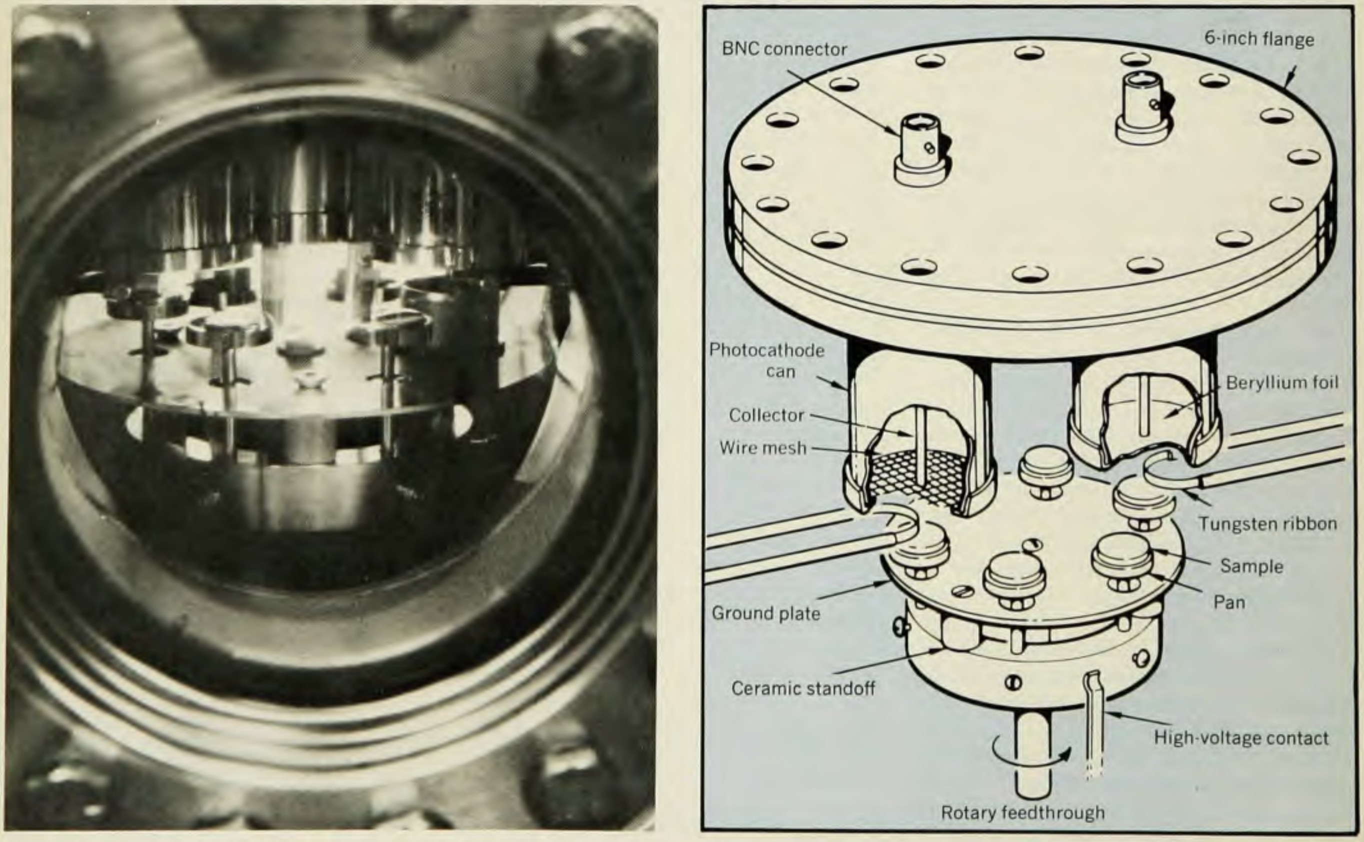
The application of Auger spectroscopy to elemental analysis has been reviewed by Chuan Chang.[5]

In the case where one or both of the final-state holes lies in the valence band, it should be possible to interpret the Auger line shape in terms of the density of states. Such an interpretation is complicated by inelastic scattering of Auger electrons on their way out of the sample, producing a step-like function with an increasing low-energy tail rather than a peak. Attempts to correct for this effect in aluminum result in a line width somewhat narrower than would be predicted from the bulk density of states.[6] This may be a consequence of band narrowing at the surface.[7] Unfortunately, few Auger spectra have been taken with the resolution required to extract this type of information. In those cases where the resolution is adequate, the line shapes sometimes do not resemble what we expect from the one-electron density of states, but instead appear more atom-like.[8] The line shape often serves as a "fingerprint" of the surface condition, however, even where it cannot be analysed in terms of a density of states.

Burdensome though inelastic scattering may be from the standpoint of line-shape analysis, it alone is responsible for the surface sensitivity of Auger spectroscopy and of the other spectroscopies I will discuss, since Auger electrons that lose more than a few electron volts in escaping from the sample do not contribute to the main peak. The principal loss mechanism for energetic electrons in a solid is the creation of "plasmons." These are quantized collective oscillations of the valence-electron fluid which sloshes about when disturbed. The sampling depth is thus determined by the mean free path for inelastic scattering. This might range from as little as 3 Å for electrons with energies below 100 eV to 30 Å at 1000 eV.[9]

Soft x-ray emission spectra

The situation is quite different in the radiative decay of a core hole. The escape depth of a soft x-ray photon is orders of magnitude greater than for an electron of the same energy. Thus, the classic method of soft x-ray band spectra is generally regarded as a bulk probe. By using grazing-incidence electrons to excite the x-rays, however, it is possible to confine the sampling depth to the outermost layers of the solid.[10] Such studies were initially undertaken to avoid the distortion of line shapes caused by self-absorption; the elimination of self-absorption is, of course, equivalent to probing only the outermost layer of a solid. This technique was exploited in 1967 by P. B. Sewell and M. Cohen to examine the composition of a surface while simultaneously studying its crystallography by reflection high-energy electron diffraction[11] (discussed by Estrup elsewhere in this issue). A month earlier, however, Roland Weber and William Peria had published news of the first use of a LEED system to obtain an Auger spectrum.[4] Auger-electron spectroscopy has since become the most popular surface analytical technique, whereas only a hand-



A soft x-ray appearance-potential spectrometer of this type has a six-sample carrousel, and the researcher has the option of detecting with or without an x-ray filter. The line drawing depicts substantially the same view as the photograph. Not shown are provisions for sputtering and vapor deposition, which are mounted on the same six-inch flange that is shown in the diagram on the right. Figure 4 ful of laboratories persist in soft x-ray emission spectroscopy of surfaces. The different reception accorded the two techniques is an indication of the relative difficulty of detecting and energy analyzing soft x rays. The soft x-ray spectrum is, however, less complex than the Auger-electron spectrum, because only two levels are involved, and the interpretation of line shapes should be correspondingly simplified (figure 1).

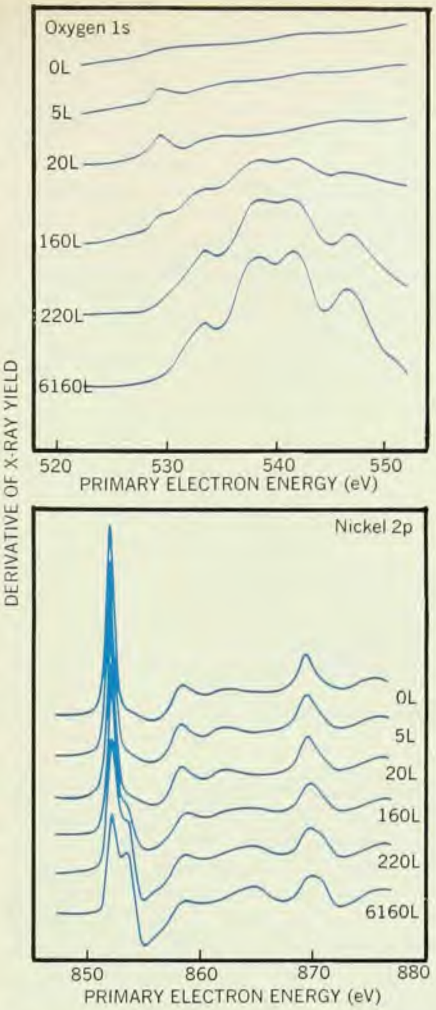
Proton-induced x rays

The technologist is inclined to regard the dependence of spectral-line shape on chemical environment as more of a hindrance than a help, because these effects are imperfectly understood and may interfere with determinations of elemental abundance. This suggests that it might be advantageous for some purposes to degrade the resolution of our spectrometers deliberately to make them insensitive to changes in line shape. If, however, we excessively degrade the resolution, the background may begin to overwhelm the signal.

The sensitivity of electron-excited soft x-ray emission, for example, is generally limited by a background of bremsstrahlung radiation produced by the radiative capture of incident fast electrons. The collision of energetic protons or alpha particles with a solid, on the other hand, results in negligible bremsstrahlung. This has led to the use of ion-induced x rays in the analysis of surface composition. Protons are used most frequently, but heavier ions may have advantages in some cases.

The comparatively weak signals encountered in proton-induced x-ray analysis rule out the use of dispersive analyzers; measurements are made instead with solid-state detectors. The current energy resolution of such detectors can reach approximately 140 eV, which rather over-achieves the objective of making the spectrum insensitive to line shape. Although it may dismay electron spectroscopists accustomed to thinking of 0.5–1.0 eV resolution, it is frequently adequate for elemental analysis,[12] as shown in figure 3.

The sensitivity of ion-induced x rays to the surface region of a solid depends on the short attenuation length of energetic ions, rather than grazing incidence as in the electron-excited case. There is, however, another way to make electron excitation sensitive to the surface. If the energy of the incident electrons is reduced to a value just above the threshold for the creation of a core hole, those incident electrons that undergo some other inelastic scattering event will no longer have sufficient energy to contribute to the production of characteristic x rays. The threshold energies for core-level excitations are in fact as characteristic of atoms as are the energies of emitted x rays or Auger electrons. This brings us to the second class of spectroscopies, those that examine the excitation of core electrons to states above the Fermi level, rather than the decay of the hole they leave behind.



The appearance-potential spectra of a nickel surface changes markedly with different oxygen exposures (L = 1×10^{-6} Torr-sec). The single-peaked oxygen spectrum at small exposures corresponds to a chemisorbed state. The multipeaked oxygen spectrum corresponds to the formation of nickel oxide. Taken from reference 16. Figure 5

Appearance-potential spectroscopy

Excitation spectroscopy has its roots early in this century when, in 1911, J. Franck and G. Hertz provided one of the first and most direct proofs of the existence of discrete atomic-energy states.[13] They determined the threshold potential for inelastic scattering of electrons from atoms in a metal vapor and correlated this threshold with the appearance of characteristic light emission. This concept was extended during the 1920's to the core levels of atoms in a solid and used to construct x-ray energy-level diagrams of the elements.[14] The method, a forerunner of modern appearance-potential spectroscopy, consisted of detecting abrupt, albeit small, changes in the total x-ray yield of an anode as a function of the applied potential. It was not a particularly sensitive method because of the large bremsstrahlung background, which tends to obscure the subtle changes in total yield that result from the excitation of characteristic x rays.

This limitation was only recently overcome with potential modulation differentiation and synchronous detection to extract the excitation thresholds from the smoothly varying bremsstrahlung background.[15] In this form soft x-ray appearance potential spectroscopy represents the highest resolution core-level spectroscopy available. It is also a remarkably simple technique—in the sense of being uncomplicated rather than easy!

Both the simplicity and the high resolution are a consequence of the fact that no dispersive analyzer is required. It is the energy of the incident electrons that is measured, and this is determined simply by the potential applied between the sample and a thermionic emitter. Thus, the resolution is ultimately limited only by the thermal spread in electron energies. The photocurrent from a metal surface exposed to x rays from the sample can serve as a measure of total x-ray yield; such a spectrometer, illustrated in figure 4, has roughly the complexity of an ion gauge. The efficiency of the photoelectric detection scheme is, however, quite low. To compensate, most researchers use incident electron currents of several milliamps. These high currents are easily achieved even at low energies since a focused beam is not required, but fragile surfaces may be destroyed by such a bombardment. More sensitive detection schemes with solid-state detectors can reduce the incident current required by two orders of magnitude,[16] and have recently been used to study the spectrum of chemisorbed gases (figure 5). In this form, appearance-potential spectroscopy may provide a test of theoretical chemisorption models such as those discussed by J. Robert Schrieffer and Paul Soven in this issue.

The principal advantage of this spectroscopy for elemental analysis, as compared to Auger and soft x-ray emission spectroscopies, is the relative simplicity of the spectrum—it consists of just the core-electron binding energies and not their term differences. Spectral features can generally be identified unambiguously from standard x-ray tables (see figure 6). There is, however, an enormous variation in sensitivity to different elements depending on the density of states above the Fermi energy, the fluorescent yield, and the oscillator strength connecting the core level to states above the Fermi energy. Thus, although appearance-potential spec-

Core-level surface spectroscopies

Spectroscopy	Probe (input)	Measurement (output)	Usual application	Principal advantage	Principal disadvantage
Recombination types					
Electron-excited Auger electron (EEAES or AES)	electron beam (≈3 keV)	derivative of electron emission current vs. emitted electron energy	elemental analysis	fast	complex spectrum
Electron-excited soft x-ray emission (SXE)	grazing incidence electron beam	x-ray emission intensity vs. wavelength	valence band states	high resolution	slow
Ion-induced x-ray (IIX or PIX)	high-energy ion beam (≈100 keV)	x-ray emission vs. x-ray energy	elemental analysis	insensitive to chemical environment	poor resolution
Excitation types					
Soft x-ray appearance potential (SXAPS or APS)	monoenergetic electrons (10–1000 ev)	derivative x-ray yield vs. incident electron energy	conduction band states	high resolution	insensitive to some elements
X-ray photoelectron (XPS or ESCA)	monochromatic x-ray beam (≈1.5 keV)	photoelectron emission current vs. electron energy	core-electron binding-energy shifts	non-destructive	complex spectrum contains both Auger and photoelectron peaks
Core-level characteristic-loss [(CL)^{2}S or IS]	monoenergetic electron beam (≈1 keV)	derivative electron emission current vs. energy loss	elemental analysis	simple spectrum	weak signal

troscopy has been used to study elements from lithium to uranium in the form of metals, semiconductors and insulators, at least two elements, palladium and gold, do not exhibit detectable thresholds with existing methods.[17]

To a first approximation the shape of an appearance-potential edge should be given by the self-convolution of the density of unoccupied states broadened by the width of the core level. The self-convolution arises because both the incident and excited core electrons must fit into the available states. This information is the conduction-band complement to that provided by the Auger electron core-valence-valence transition for the valence band. Because the core state overlaps only part of the valence and conduction bands, these techniques respond to the local chemical environment experienced by the atom. The interpretation of line shapes is complicated by broadening introduced by the finite lifetime of the core hole, the screening response of the conduction electrons to the suddenly altered core potential and variations in the magnitude of the atomic-matrix elements which completely suppress some thresholds.

The position of the edge, as well as its shape, can be measurably influenced by changes in chemical configuration. These "chemical shifts" are small compared to the binding energies and do not seriously interfere with elemental identification. They do, however, offer some insight into the local electronic environment.

Variations in the density of states near the Fermi level can distort the shape of the edge and complicate the determination of threshold excitation energies. This can be avoided by measuring the kinetic energy of core electrons that have been excited into states far above the Fermi energy, where the density is so slowly varying that it can be regarded as a constant. This is done in a technique that traces its genealogy back even further than appearance-potential spectroscopy.

X-ray photoelectron spectroscopy

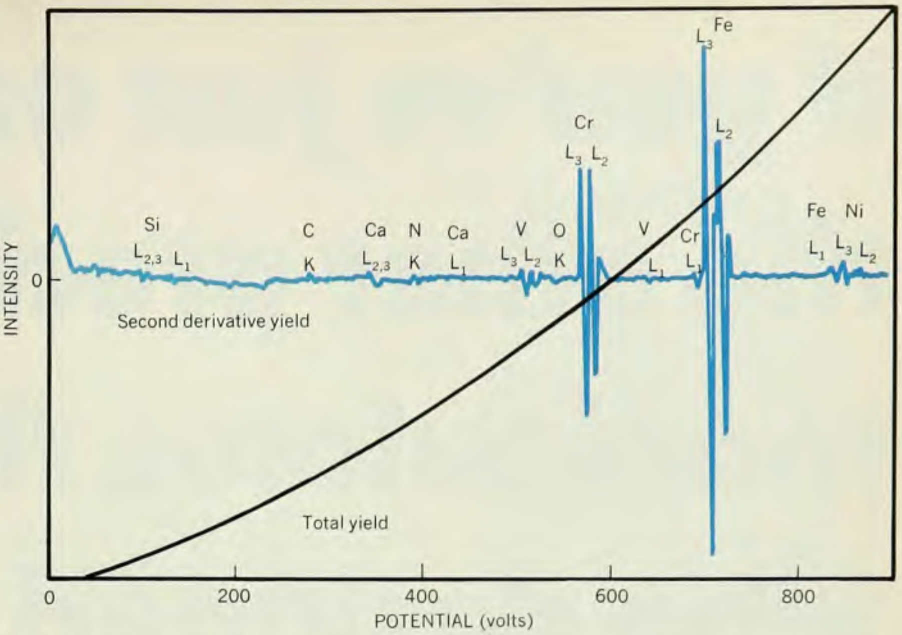
Commenting on work begun with W. F. Rawlinson in 1914,[18] H. Robinson wrote that "primary x-radiation of a sufficiently high single frequency gives rise to what may be called a 'line spectrum' of secondary corpuscular rays from the target, this line spectrum being composed of groups of electrons from the different levels in the atoms" (figure 7). The revival of x-ray photoelectron spectroscopy (or electron spectroscopy for chemical analysis, ESCA) in recent years[19] stems from technological innovations that alleviate many of the experimental constraints suffered by Robinson, and theoretical advances that extend the usefulness of the information obtained. Although Eastman and Nathan discuss x-ray photoelectron spectroscopy in detail elsewhere in this issue, I wish to describe it here to place it with respect to the other core-level spectroscopies.

If a core electron absorbs the energy of an incident photon, it may be ejected into the vacuum where its kinetic energy can be related to the binding energy of the core state (figure 1). This assumes that we can identify those emitted electrons that have not undergone inelastic collisions on their way out of the sample; for most emitted electrons this is not the case. On the low kinetic-energy side of each photoelectron peak (figure 8) the background rises as a result of what Robinson called "straggling." (The photoelectron spectrum, incidently, also has the Auger spectrum superimposed on it, and the straggling phenomenon affects the Auger lines just as it does the photoelectron lines.) Only the relatively few electrons contained in the sharp peaks have escaped without inelastic collision and must therefore have originated very near the surface.

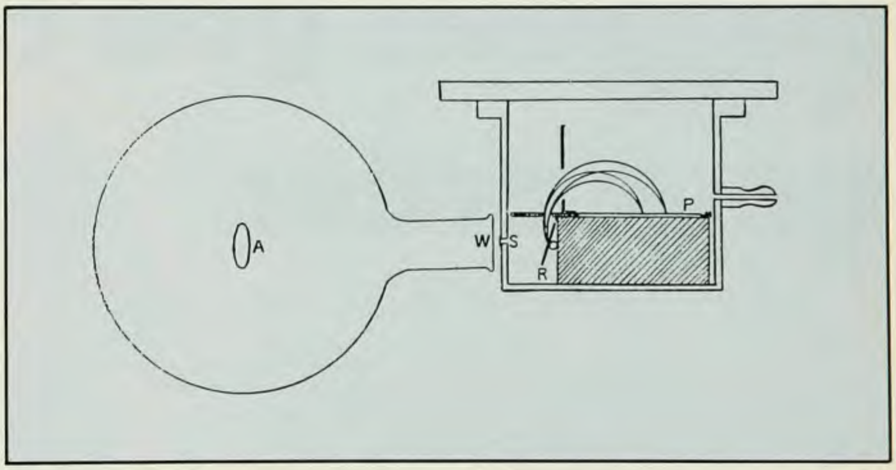
Since the core-level transitions in x-ray photoelectron spectroscopy do not involve states near the Fermi energy, the shapes of the peaks are relatively unaffected by chemical environment. It is of course possible to study those electrons excited directly out of the valence band, but the line shape is not then specific to a particular element. The emphasis has therefore been on the measurement of binding-energy shifts. Binding energies obtained by x-ray photoelectron and appearance-potential spectroscopies are equal to within experimental error.[20] The interpretation of binding-energy shifts in terms of charge transfer, however, requires a knowledge of bond lengths and angles. This interdependence between the determination of electronic structure and surface crystallography complicates the surface-characterization problem more than is generally recognized.[21]

Characteristic-loss spectroscopy

A simple thermionic emitter and a voltage supply can provide a source of ionizing particles more intense and



Appearance-potential spectroscopy has been used to show that high-temperature annealing of stainless steel results in surface depletion of chromium, thereby lowering its corrosion resistance. Differentiation allowed the peaks to stand out from the total x-ray yield. Figure 6



A vintage photoelectron spectrometer, from a 1914 paper by H. Robinson and W. F. Rawlinson, shows many parts that are fundamental to modern machines. A is the anode of the x-ray tube, W is an aluminum window, S is a defining slit covered with mica, R is the sample being studied and P is a photographic plate on which the photoelectron lines, bent by a magnetic field, are recorded. The paper appeared in the *Philosophical Magazine.* Figure 7

monochromatic than the x-ray sources conventionally used in electron spectroscopy for chemical analysis. Why not do the ESCA experiment with incident electrons rather than photons?

Alas, unlike x-ray photons, an incident electron is not constrained to yield all its kinetic energy when it scatters from an inner shell. Instead, the incident electron may be captured in a state above the Fermi level and give up only a fraction of its energy to the core electron. Thus, in contrast to the XPS case, where core levels give rise to distinct peaks in the energy distribution of emitted electrons, excitation by electron bombardment produces only a weak edge corresponding to the case in which the incident electron is captured at the Fermi energy.

Although extremely weak compared to photoelectron peaks, the shape of the characteristic-loss edge should, to a first approximation, correspond to the density of unoccupied states. That is, it should look very much like an x-ray absorption edge. The characteristic-loss edge in the back-scattered spectrum, however, reflects the electronic structure in only the outermost few atomic layers.

Unfortunately the strong electron–electron interaction, which is responsible for this surface sensitivity, has a less desirable effect. The sky above the sample is thick with secondary electrons, very few of which have been scattered from inner electron shells. We would expect that taking the derivative of the spectrum would help us to extract the core-level characteristic-loss edges from this background, and indeed, Harris recognized their presence in his original Auger-electron spectra.[2]

The characteristic-loss edges, however, are generally much weaker and far less abundant than the Auger peaks. Therefore, to make much use of these edges they must first be distinguished from the Auger spectrum in which they are immersed. This distinction depends on the fact that characteristic-loss features are fixed relative to the incident-electron energy. The Auger features, on the other hand, are fixed relative to the Fermi energy of the sample and are thus independent of the energy of the incident electrons. Robert Gerlach exploited this by superimposing a small oscillation on the primary-electron energy and detecting only those features in the secondary-electron spectrum that varied synchronously.[22] At this point the sensitivity of characteristic-loss spectroscopy to electronic structure has not been widely exploited although it has been used to resolve ambiguities in Auger-electron spectra.[23]

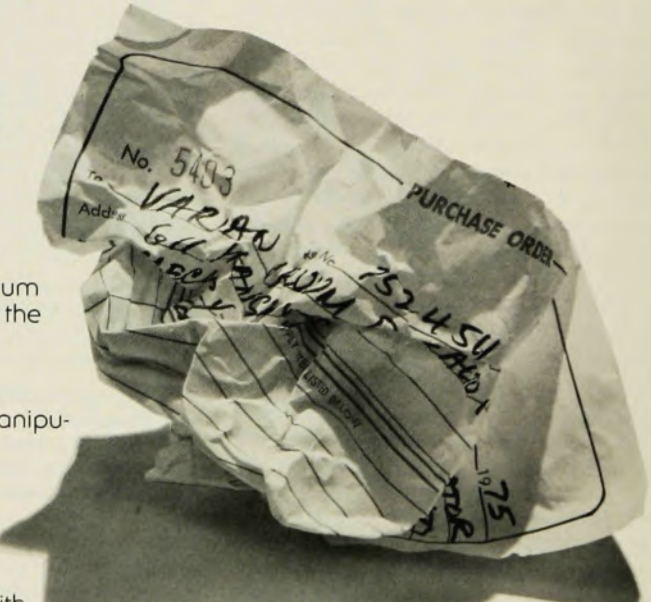
The many-body problem

Soft x-ray spectra of the alkali metals were once regarded as a major triumph of the free-electron theory of metals.[24] As we become more sophisticated, however, we discover reasons why a simple one-electron band model should not be expected to explain adequately transitions involving the core levels. Such models ignore the screening response of the conduction electrons to the core hole that was suddenly created or annihilated.[25] For surface spectroscopies, the predicted consequences of this dynamic screening include singular behavior near thresholds,[26] strong plasmon satellites,[27] skewed line shapes[28] and a screening energy correction to the core-electron binding energy.[29] However, despite all the theoretical stew over these many-body effects, incontrovertible experimental evidence of their existence is lacking.

Scorekeeping

John Fortesque wrote in 1471 that "comparisons are odious" and the passage of five centuries has not made them less so. It is difficult even to distinguish the limitations of techniques from the limitations of the scientists who employ them ("In unskilled hands a Stradivarius is just a fiddle"). I shall therefore make no attempt to rank the core-level surface spectroscopies. Each provides somewhat different information, and each is hampered by its own unique uncertainties. It is not possible to discuss their relative merits until the

If you've just ordered the other precision manipulator, the man who designed it suggests you cancel your order.



When Lynn ("Buzz") Alton designed Varian's precision vacuum manipulator a few years ago, it won an IR-100 award for the most versatile and precise device of its kind.

That's what Buzz meant it to be.

And it was. **Was** . . .

Now Buzz has designed a new, ultra-high precision manipulator that obsoletes the old one.

It will wear a Huntington nameplate. Because Buzz joined us last year and has been working on the design ever since.

It is the most precise, most versatile manipulator available anywhere. **Is** . . .

Buzz's new manipulator will position work samples with micrometer precision and repeatability on **all axes** . . . is the only manipulator with micrometer **tilt motion** . . . and flip actuator position repeatability is **50 times greater**, position resolution is **5 times greater**, and linear motion is **30% greater.**

But those are just openers. You can apply the same kind of multiples to **rotary motion** and **translation** . . . a **motor drive** is available for X, Y, Z, and rotation . . . and construction is **modular** so that you can buy what you need now, grow with it later.

And, believe it or not, it's **lower priced!**

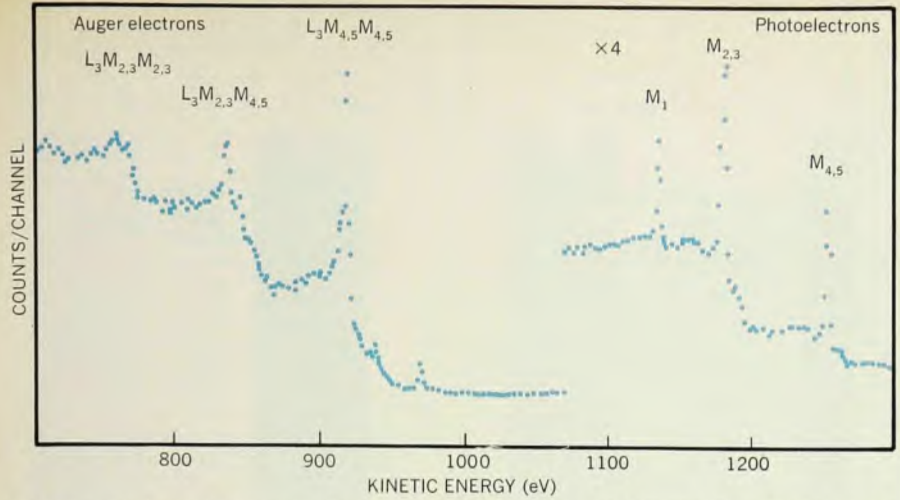
There's still a lot more to it. Cancel that Varian order, then call or write us today for full details.

Oh, yes. If you've already bought Buzz's older design, we know how you feel. So we've built a retrofit kit to upgrade your Varian model to the Huntington model (all parts and accessories are interchangeable).

Buzz wouldn't have it any other way.

Huntington
Laboratories Inc.
1400 Stierlin Road
Mountain View, California 94043
(415) 964-3323 TWX 910-379-6944

Circle No. 30 on Reader Service Card



The x-ray photoelectron spectrum of a copper surface has peaks resulting from ejected core electrons *and* peaks from Auger electrons, produced by non-radiative decay of core holes. The surface was irradiated by Mg K_α radiation. On the low-kinetic-energy side of each photoelectron peak the background rises due to the straggling electrons, which have been inelastically scattered on their way out of the sample. The spectrum was taken by Lo I Yin of the NASA-Goddard Space Flight Center, Green Belt, Maryland. Figure 8

problems they are expected to solve are clearly defined.

There is, for example, a widespread misapprehension that we should be able to define the surface composition by attaching a percentage to each element as we do for homogeneous bulk samples. The surface is by its nature inhomogeneous along its normal, and its "composition" has a precise meaning only if we are able to specify its structure. Thus, extravagant claims of "quantitative" surface analysis[5] are rooted in an unclear notion of the problem.

It appears that as each technique is discovered (or rediscovered) it must go through a period of contrived enthusiasm during which it is extolled as a cure for every infirmity. The important point is that we have at our disposal a variety of spectroscopies that responds to the local electronic environment of atoms in the surface region of a solid. Each of these spectroscopies views the surface from a somewhat different perspective. The task of the surface physicist is to reconcile these different viewpoints. It is a task that has hardly begun.

References

1. J. J. Lander, Phys. Rev. **91**, 1382 (1953).
2. L. A. Harris, J. Appl. Phys. **39**, 1419 (1968).
3. P. W. Palmberg, J. Vac. Sci. Technol. **12**, 369 (1975).
4. R. E. Weber, W. T. Peria, J. Appl. Phys. **38**, 4355 (1967).
5. C. C. Chang in *Characterization of Solid Surfaces*, (P. F. Kane, G. B. Larrabee, eds.) Plenum, New York (1974).
6. J. E. Houston, J. Vac. Sci. Technol. **12**, 255 (1975).
7. J. W. Gadzuk, Phys. Rev. B **9**, 1978 (1974).
8. C. J. Powell, Phys. Rev. Lett. **30**, 1169 (1973); L. Yin, I. Adler, T. Tsang, M. H. Chen, D. A. Ringers, B. Crasemann, Phys. Rev. A **9**, 1070 (1974).
9. C. J. Powell, Surf. Sci. **44**, 29 (1974).
10. J. R. Cuthill in *X-Ray Spectroscopy*, (L. V. Azaroff, ed.) McGraw-Hill, New York (1974).
11. P. B. Sewell, M. Cohen, Appl. Phys. Lett. **11**, 298 (1967).
12. W. Bauer, R. G. Musket, Appl. Phys. Lett. **20**, 411 (1972).
13. J. Franck, G. Hertz, Verh. Dtsch. Phys. Ges. **16**, 12 (1911).
14. O. W. Richardson, C. B. Bazzoni, Philos. Mag. **42**, 1015 (1921).
15. R. L. Park, J. E. Houston, J. Vac. Sci. Technol. **11**, 1 (1974).
16. S. Andersson, H. Hammarqvist, C. Nyberg, Rev. Sci. Instrum. **45**, 877 (1974).
17. R. L. Park, Surf. Sci. (in press).
18. H. Robinson, W. F. Rawlinson, Philos. Mag. **28**, 277 (1914).
19. D. A. Shirley, J. Vac. Sci. Technol. **12**, 280; T. A. Carlson, PHYSICS TODAY, January 1972, page 30.
20. C. Webb, P. M. Williams, Phys. Rev. Lett. **33**, 824 (1974).
21. C. B. Duke, R. L. Park, PHYSICS TODAY, August 1972, page 23.
22. R. L. Gerlach, J. E. Houston, R. L. Park, Appl. Phys. Lett. **16**, 179 (1970).
23. R. L. Gerlach, J. Vac. Sci. Technol. **8**, 599 (1971).
24. H. M. O'Bryan, H. W. P. Skinner, Phys. Rev. **45**, 370 (1934).
25. G. D. Mahan, Phys. Rev. **163**, 612 (1967).
26. M. Natta, P. Joyes, J. Phys. Chem. Solids **31**, 447 (1970); G. E. Laramore, Phys. Rev. Lett. **27**, 1050 (1971).
27. D. C. Langreth, Phys. Rev. Lett. **26**, 1229 (1971); G. E. Laramore, Solid State Commun. **10**, 85 (1972).
28. S. Doniach, M. Šunjić, J. Phys. C **3**, 285 (1970).
29. G. E. Laramore, W. J. Camp, Phys. Rev. B **9**, 3270 (1974). □