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Solid-State Photoelectron Spectroscopy with Synchrotron Radiation

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Summary. Synchrotron radiation sources, providing intense, tunable, polarized, and stable beams of ultraviolet and x-ray photons, are having a great impact on biology, physics, chemistry, materials science, and other areas of research. Synchrotron radiation has revolutionized solid-state photoelectron spectroscopy by enhancing its capabilities for investigating the electronic behavior of solids and solid surfaces. Several fundamental photoemission techniques that rely on synchrotron radiation are discussed in this article. These techniques have an adjustable tunable surface sensitivity and provide the first direct mapping of the electronic band structure. Recent applications of photoelectron spectroscopy for studies of chemisorption geometries and surface structures are discussed.

The radiation emitted by electrons circulating in a synchrotron or in a storage ring is a powerful probe with which to examine a variety of fundamental biological, chemical, and physical phenomena. In this article we examine photoelectron spectroscopy, one of the many techniques of modern science profiting from synchrotron radiation (*1*). We discuss how photoelectron spectroscopy is used to reveal the behavior of electrons in solids and surface structural properties. Most of the fundamental properties of condensed matter can be predicted on the basis of a quantitative understanding of the behavior of its electrons. Within the last few years, scientists using synchrotron radiation in their studies have made important breakthroughs. For example, the results of their experiments have been used to refine the fundamental models describing the electronic behavior in solids. Additional synchrotron radiation facilities, which will come on-line around the United States and abroad within the next 1 to 4 years, will further accelerate this progress.

Modern photoelectron spectroscopy is a direct outgrowth of a phenomenon explained by Einstein in 1905: A photon, or quantum of electromagnetic radiation, is absorbed in a solid (or liquid or gas), and an electron is excited from its unperturbed initial state to a state of higher energy. If the excited electron is close enough to the surface and is energetic enough, it has a chance of moving to the surface and escaping from the solid. It is then a "photoelectron." These photoelectrons can be analyzed outside the solid to determine their energy and momentum, quantities that determine their "state." One can then extrapolate backward to characterize states of the electrons inside the solid. A broad knowledge of the electronic properties or energy states of the solid can be achieved in this way.

Photoelectron spectroscopy poses many technical challenges in its practical applications. A major problem is finding a suitable photon source. The electron must obtain from the photon enough energy to overcome the barrier binding it to the solid. Photon energies suitable for photoelectron production are in the ultraviolet and x-ray ranges, approximately between a few electron volts and several kiloelectron volts (1 eV corresponds to a wavelength of 1.24×10^{-6} meter or a wave number of 8066 reciprocal centimeters). Before the use of synchrotron radiation in the late 1960's, only conventional ultraviolet gas discharge or x-ray emission sources were available, and these suffered from various technical limitations.

Synchrotron Radiation: A Unique Source of Photons

Synchrotron radiation has evolved from being an undesirable but unavoidable by-product of particle accelerators to being a highly desirable experimental tool. It results naturally from the centripetal acceleration of charged particles moving at relativistic velocities inside an accelerator, such as a synchrotron. In a storage ring, for example, electrons are accelerated to energies of mega- or gigaelectron volts and held in stable orbits for long periods of time, the energy lost in the form of synchrotron radiation being restored by radio-frequency accelerating cavities. Whenever the orbit is curved, the electrons are instantaneously centripetally accelerated and emit electromagnetic radiation, or photons, in a direction tangent to the orbit. The emitted electromagnetic radiation has the following unique properties:

1) Intense synchrotron radiation is emitted in a spectral continuum of photon energies extending from the x-ray range through the ultraviolet and the visible and into the infrared range. The high-photon-energy limit of the synchrotron radiation spectrum is determined by the energy of the emitting electrons and by the curvature of their orbits. No other spectrally continuous source of photons spans this wide range. The emission spectra of the two photon sources of the University of Wisconsin Synchrotron Radiation Center are shown in Fig. 1 to demonstrate the intense continuum character of synchrotron radiation. Tantalus

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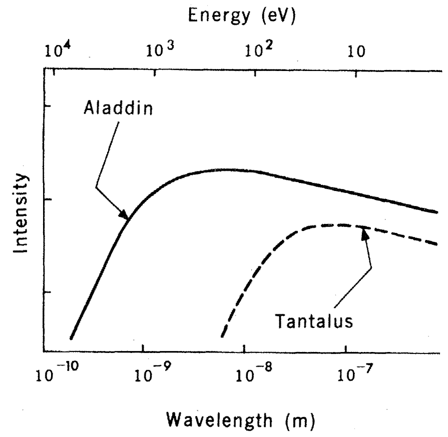


Fig. 1. Emission spectra of the two photon sources of the University of Wisconsin Synchrotron Radiation Center. Tantalus, a 240-MeV electron storage ring, has been in operation since the late 1960's. Aladdin, a 1-GeV storage ring, will be commissioned in 1980. The spectra are plotted on a log-log scale. The expected peak emission of Aladdin for a circulating electron beam of 100 mA is approximately 2.5×10^{12} photons per second in a 1-milliradian horizontal aperture with a photon energy bandwidth of 0.3 eV.

has been in operation as a full-time photon source since the late 1960's and was the first storage ring used as a source of synchrotron radiation. Aladdin is a higher energy (1 GeV compared to 240 MeV) storage ring that is under construction and is due to be commissioned in 12 to 18 months. Other U.S. radiation facilities are in operation at the National Bureau of Standards and Stanford University, and two additional U.S. facilities are under construction at Cornell and Brookhaven National Laboratory. Several other facilities are in operation or under construction in Europe and Japan. In each case, the spectral output is qualitatively similar to those shown in Fig. 1, although the high-energy cutoff varies from machine to machine.

2) Synchrotron radiation is highly polarized with its electric field vector lying in the plane of the electron orbit.

3) Synchrotron radiation is a "clean" source because the emitting electrons circulate in the storage ring under ultrahigh vacuum conditions. These conditions are ideal for any experimental technique requiring ultrahigh vacuum, such as photoelectron spectroscopy.

4) Synchrotron radiation is highly collimated in the vertical plane, and most of the radiation can be collected and focused with optical focusing elements.

5) The synchrotron radiation is emitted in discrete bursts, each lasting a few nanoseconds. This time structure results from the passage of electron bunches through the source points within the storage ring magnets.

Each of these features is used to advantage in many different experimental techniques involving synchrotron radiation. We discuss here their important role in photoelectron spectroscopy.

Why Synchrotron Radiation Is Crucial

A photoemission experiment consists of measuring the number of emitted photoelectrons per incident photon as a function of the parameters characterizing the photoemission process. The most important of these parameters are the energy and polarization of the photon and the energy and momentum of the emitted electron. Ideally, in a photoemission experiment, one should be able to control all these parameters. Photon energy and polarization, however, cannot be controlled when a conventional ultraviolet or soft-x-ray source is used because these "line sources" emit unpolarized photons with fixed energy. The enhanced flexibility offered by a tunable, polarized source has resulted in great demand for synchrotron radiation. Scientists involved in photoemission experiments account for a large share of the total demand for synchrotron radiation in the United States and elsewhere. Many new photoemission techniques have been developed in recent years, totally or partially relying on the use of synchrotron radiation.

A Tunable Surface Sensitivity

In a photoemission process, two things must occur: the photon must be absorbed and the excited electron must reach the surface and escape. Only electrons excited within the first few atomic layers have a reasonable probability of escaping from the solid before suffering energy losses. Electrons excited deeper in the solid will scatter inelastically, losing initial-state information and possibly decaying to an energy too low for escape. Hence, photoelectron spectroscopy emphasizes the properties of electrons near the surface. These electrons are extremely important since they are involved in such fundamental chemical processes as chemisorption, catalytic reactions, corrosion, passivation, and the formation of interfaces (as in solid-state devices). The thickness of the region probed by photoemission (that is, the average depth from which "primary" photoelectrons come) depends on the photoelectron energy (*2*) as shown in Fig. 2. In turn, this energy is determined by the photon energy. Synchrotron radiation makes it possible to select photon energy to emphasize or de-emphasize the surface sensitivity of photoelectron spectroscopy. R. Z. Bachrach and co-workers from Xerox (*3*) and M. M. Traum, Z. Hurych, and co-workers from Bell Laboratories and Northern Illinois University (*4*) have recently shown that surface effects can be emphasized or de-emphasized in this way.

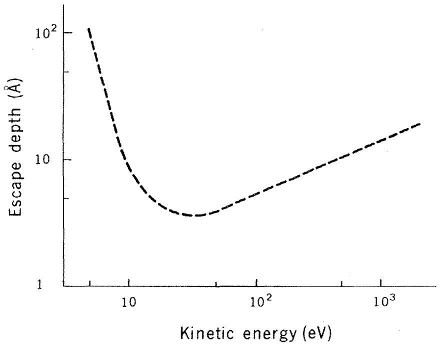


Fig. 2. Escape depth of photoelectrons from solids as a function of their kinetic energy in a vacuum (*2*). This curve is an average of escape depth data for many materials. Escape depth curves are different for different materials but are qualitatively similar to the one shown here. The broad minimum corresponds to the maximum surface sensitivity of photoelectron spectroscopy techniques.

Probing the Distribution in Energy of the Electrons

Most of the chemical and physical properties of a solid are related to the distribution in energy of its electrons. In an isolated atom the allowed energies for an electron form an ordered set of discrete levels. When atoms are brought together to form a solid, the core electrons, whose orbitals are close to the nucleus, retain most of their atomic properties. The outermost electrons extend greater distances from the nucleus, are less tightly bound, and, because they "feel" the potential of the neighboring nuclei, their properties are strongly modified. Their energy levels are broadened to form bands of allowed energies separated by forbidden gaps. All of the electronic states of the solid—atomic-like core levels and band states—are occupied to an energy called the Fermi energy; above the Fermi energy, the states are empty.

In the photoemission process, the electron is excited from an occupied state below the Fermi energy to a state in an empty band. Its final energy is increased with respect to its initial energy by an amount equal to the energy of the absorbed photon, $h\nu$. The distribution in energy of the photoelectrons outside the solid will be an image of their initial distribution in energy inside the solid displaced by $h\nu$ as shown in Fig. 3. A plot of the number of photoelectrons as a function of their kinetic energy for a fixed photon energy is called an energy distribution curve. The energy distribution curves reflect the distribution in energy of the occupied states of the solid, the so-called density of states.

The first energy distribution curve recorded with synchrotron radiation was published by Eastman and Grobman (5) in 1972. Results of a density of states study for a solid of considerable current interest are illustrated in Fig. 4, where the calculated density of states for yttrium dihydride, a representative metal-hydrogen system, is compared to an energy distribution curve recently measured with synchrotron radiation (6). The good agreement supports the model used to describe an "alloy" of a transition metal and the lightest of atoms, hydrogen. The broad emission feature well below the Fermi energy, E_F, represents a band of states not observed in the elemental metal but indicative of metal-hydrogen interactions.

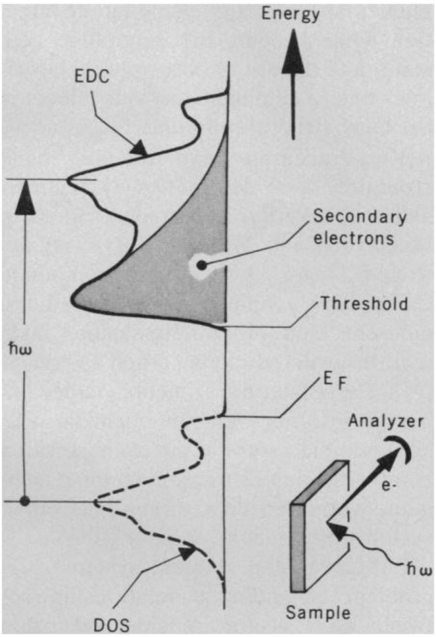


Fig. 3. Schematic diagram of photoelectron spectroscopy. Tunable synchrotron radiation of energy $\hbar\omega$ is incident on the sample and generates photoelectrons. The photoelectrons are collected and their kinetic energies analyzed to obtain an energy distribution curve (*EDC*) as shown. To a first approximation, the energy distribution curve corresponds to the distribution in energy of the electrons in the solid or initial density of states (*DOS*) shifted by an energy $\hbar\omega$. It includes a contribution from "secondary" photoelectrons, or electrons that have scattered inelastically before emission.

Energy distribution curves emphasize the occupied electronic states. The empty states can be effectively investigated by a different photoemission technique, constant initial state spectroscopy, introduced by Lapeyre and co-workers (7) in 1974. The constant initial state technique requires a tunable photon source and therefore is possible only with synchrotron radiation. In a constant initial state experiment, the monochromator, which is used to select the photon energy, is scanned synchronously with the electron energy analyzer. In this way, the analyzer is forced to accept only electrons arising from an initial state of chosen energy. The number of those electrons depends primarily on the density of unoccupied states to which the electron can be excited when it absorbs the photon. A constant initial state spectrum, therefore, maps the density of states above the Fermi energy and gives information complementary to that obtained through an energy distribution curve study.

As an example of the constant initial state technique, we show in Fig. 5 three representative spectra obtained through synchrotron radiation studies of potassium chloride (7). The two prominent peaks at 9.7 and 12.6 eV correspond to features in the empty density of states. The constant initial state technique has recently been valuable in studying the energy states of bulk materials and chemisorbed overlayers (7-9). Use of minicomputer-controlled monochromators at synchrotron radiation facilities simplifies this technique and, within the last few years, has made the study of unoccupied states a routine practice.

A Direct Experimental Look at the Band Structure

For many years the existence of allowed bands and forbidden gaps, discussed in the previous section, has been regarded by solid-state theorists to be a consequence of the energy band structure of the solid. The soundness of this conceptual framework has only recently been directly proved, and this has been done with angle-resolved photoelectron spectroscopy.

Quantum mechanics describes particles by means of wave functions. For example, an electron moving in free space is described by a plane wave—that is, by a wave function of the form:

$$\psi(\mathbf{r}, t) = u \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] \quad (1)$$

where u is a constant, $\mathbf{r}$ is the space coordinate, t is the time, ω is the (angular) frequency, and $\mathbf{k}$ is the wave vector. Frequency ω and wave vector $\mathbf{k}$ are related to the energy E and the momentum $\mathbf{p}$ of the particle by the de Broglie equations:

$$E = \hbar\omega; \ \mathbf{p} = \hbar\mathbf{k} \quad (2)$$

where $\hbar$ is Planck's constant divided by 2π. For a free electron the energy is entirely kinetic and is related to the magnitude of the momentum by $E = p^2/2m$, or

$$E = (\hbar k)^2/2m \quad (3)$$

where m is the electron mass. A photon or quantum of electromagnetic radiation is also described by a plane wave and obeys the de Broglie equations. Frequency and wave vector are now related by $\omega = ck$, where c is the velocity of light. Thus, according to Eq. 2

$$E = c\hbar k \quad (4)$$

A plot of energy versus wave vector is called a dispersion curve. Equation 3 defines the dispersion curve characteristic of a free electron. Equation 4 gives the

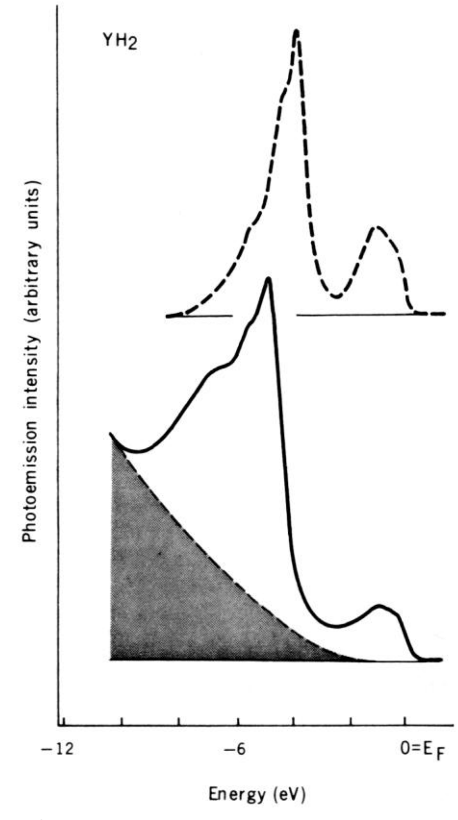


Fig. 4. Energy distribution curve (solid line) taken on YH_2 with a photon energy of 23 eV (6). The shaded area underneath this curve shows the estimated background due to inelastically scattered secondary photoelectrons. The features of the energy distribution curve are reproduced by the calculated density of states of the crystal (dashed curve). The broad band extending between 3 and 10 eV below the Fermi energy, E_F, reflects hydrogen-metal interactions.

dispersion curve describing the motion of a photon.

Dispersion curves also describe electrons moving within a crystalline solid. These are not free particles because they feel and react to the strong, periodic potential of the crystal (for example, the electrostatic potential of the ions forming a periodic array in an ionic crystal). The wave functions describing these electrons retain some of the free-electron plane wave features, and the general wave function form for electrons in a crystal is the Bloch wave

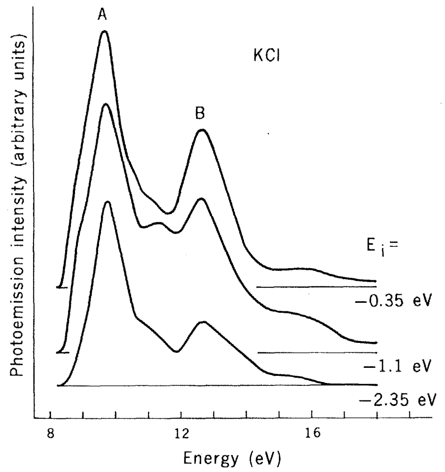
$$\psi(\mathbf{r}, t) = u_{\mathbf{k}}(r)\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \quad (5)$$

where $u_{\mathbf{k}}(\mathbf{r})$ is no longer a constant but is a periodic function of **r** having the same periodicity as the crystal. There is now no simple relationship between energy and wave vector, and the motion of the electrons in the crystal is characterized by complicated dispersion curves. The solid lines in Fig. 6 show, for example, the calculated dispersion curves, $E(k)$, for a perfectly ordered crystal of copper along different directions of the wave vector (*10*).

In solid-state physics the dispersion curves in all the possible wave vector directions form the energy band structure of the crystal. It is evident from Fig. 6 that the allowed energies (that is, the energies related by the dispersion curves to one or more wave vectors) do not appear as isolated levels but rather form allowed bands. There are energies that do not correspond to any wave vector, and these are energies that an electron in the solid cannot have—energies in a forbidden gap. Thus, the band structure of a crystalline solid results in the existence of allowed bands and forbidden gaps.

Other particles or quasi particles traveling through the crystal see a periodic potential and have a band structure. For example, a band structure can describe the motion of phonons, the quasi particles associated with the elastic vibrations of the atoms forming the crystal. This phonon band structure can be directly probed by use of neutron scattering. Photons can be used to probe the electronic dispersion curves through angle-resolved photoelectron spectroscopy. The development of this fundamental technique, beginning in about 1973, has made it possible to directly map the electronic band structure.

Mapping the electronic band structure requires measuring dispersion curves—that is, energies and wave vectors of the electrons. In any photoemission experiment the energy of the photelectron is measured outside the solid. The magnitude of its wave vector then follows from Eq. 3. In an angle-resolved photoemission measurement, only electrons emitted in a well-defined direction from a single crystal are energy-analyzed. This determines both the magnitude and the direction of the wave vector outside the solid. Mapping the dispersion curve, however, requires determining the energy and wave vector inside rather than outside the solid. Relating wave vectors inside and outside the solid is not a trivial problem since, on crossing the solid-vacuum interface, the energy is conserved but the wave vector changes—only its component parallel to the surface, $k_{\parallel}$, is left unchanged. Smith and Traum (*11*), employed layered two-dimensional crystals (where $k_{\parallel}$ was the only important component of **k**) as pilot systems for experimental plots of the $E(k)$ curves along directions parallel to the layers.



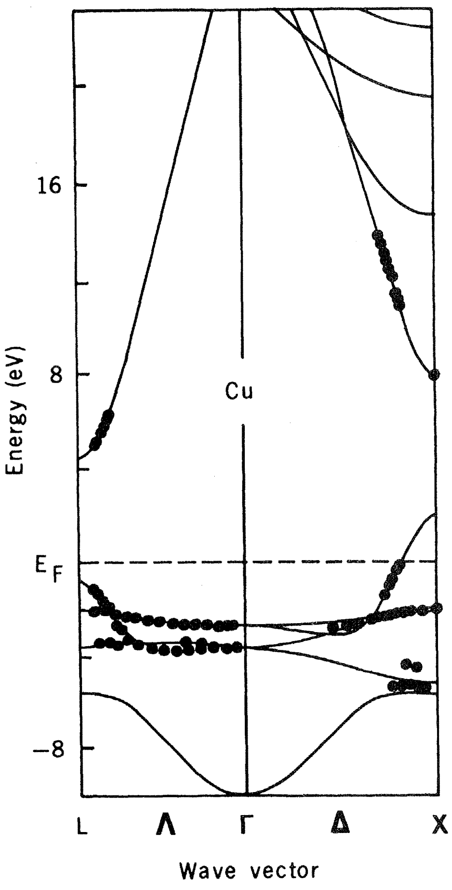


Fig. 5. Constant initial state spectra taken by Lapeyre and co-workers on potassium chloride (*7*). The sharp peaks A and B reflect features in the empty density of states of the crystal. The three spectra were taken with three different choices of the (constant) initial-state energy E_i, specified at the right-hand side of each curve. Energies are measured from the top of the valence band. Fig. 6. Solid lines show the calculated (*10*) dispersion curves, $E(k)$, of copper. These curves are plotted along the two high-symmetry crystalline directions of **k**, the wave vector. The dots are experimental points (*18, 19*) mapping the band structure of this crystal. They were obtained by angle-resolved photoelectron spectroscopy with synchrotron radiation.

Since 1974, band structure mapping techniques have evolved rapidly. Once again, access to synchrotron radiation sources has been crucial because a tunable photon source allows one to change the wave vector component parallel to the surface by changing the magnitude of the wave vector (that is, the electron kinetic energy) while keeping its direction constant. This approach is complementary to that of changing the direction while keeping the magnitude constant, and the use of both approaches allows one to eliminate spurious effects of the band structure plotting.

Very accurate experimental band structures were determined by Williams and co-workers (*12*), Larsen *et al.* (*13*), McGovern and Williams (*14*), and Petroff (*15*) for the layered compound GaSe. This technique was extended to a different kind of two-dimensional system, an ordered chemisorbed overlayer (*16*). These later experiments yielded important information about chemisorption sites and the nature of the chemisorption bonds. The band structure mapping technique was extended to three-dimensional systems by Grandke *et al.* (*17*).

For three-dimensional systems the problem of finding a relationship between wave vectors outside and inside the solid is overcome by a simultaneous use of theory and experiment. For example, Knapp *et al.* (*18*) and Dietz and Eastman (*19*) recently mapped the band structure of copper above and below the Fermi energy. The experimentally determined (E,k) points are shown in Fig. 6. The extremely good agreement between theory and experiment for copper emphasizes what can, in principle, be done with crystalline materials or ordered chemisorbed overlayers.

Studying Geometrical Properties

The investigation of geometrical properties—for example, of crystal structures—is a fundamental problem of the physics and chemistry of condensed matter. A very sophisticated and reliable technique, x-ray crystallography, is used to study bulk structural properties. Studies of surface structures present different kinds of technological problems, the most obvious of which is that the probe must be surface-sensitive. Photoelectron spectroscopy, with its built-in surface sensitivity, is making fundamental contributions to this field.

The photoemission techniques developed to investigate surface geometries can be divided into two broad categories: approaches based on the study of the valence electrons and approaches based on the study of photoionization cross sections. The valence electrons are engaged in the formation of chemical bonds and the properties of those bonds strongly depend on the structure of the system. Therefore the study of valence electrons provides indirect information about surface geometries. The information provided by photoionization cross-section studies is more immediate, since the geometrical properties directly modulate the cross section.

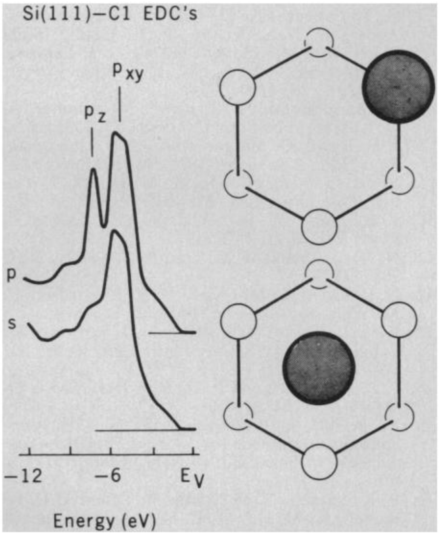


Fig. 7. Chemisorption site identification by photon polarization effects in the photoelectron spectra. A chlorine atom (shaded circle) chemisorbed on a Si(111) surface can be expected to sit in either a onefold-symmetric site (top right) or a threefold-symmetric site (bottom right). When in the onefold site, the Cl atom sits above one of the top layer Si atoms and its *p* electrons are engaged in Cl-Si bonds pointing in the *z* direction, perpendicular to the surface. The p_z electrons in this configuration lie at lower energies than the p_x and p_y electrons. The contrary is true for the threefold site. The energy distribution curves by Rowe and co-workers (*9*) (left side) exhibit two sharp peaks due to Cl *p* electrons. The intensity of the lower-energy peak dramatically decreases when the photon polarization is such that the electric field vector of the photon is parallel to the surface (*s* polarization). This behavior is typical of p_z electrons. The p_z electrons are thereby experimentally shown to be at a lower energy than the p_x and p_y electrons, and this identifies the onefold site as the correct chemisorption site for Cl on Si(111).

The structure of the system influences both the position in energy of the valence electron states and their atomic orbital character. The atomic orbital character is often reflected in the photon polarization dependence of the emission peaks in the energy distribution curve (*20*). Photon polarization effects can be easily studied using the natural polarization of the synchrotron radiation source. Rowe and co-workers (*9*), for example, were able to identify the chemisorption site for chlorine atoms on silicon and germanium surfaces by studying the photon polarization-induced changes in the energy distribution curves shown in Fig. 7.

Chemisorption sites have been identified by means of angle-resolved photoemission—for example, by the band structure mapping described in the previous section (*16*). Different hypothetical chemisorption sites give remarkably different theoretical band structures for an ordered chemisorbed overlayer. The experimental $E(k)$ plots allow one to identify the correct chemisorption geometry.

Use of cross-section measurements to study chemisorption geometries was pioneered by Plummer and Gustaffson and their co-workers (*21*). Many experimenters in this field examine the photoionization cross section of core levels that correspond to a well-characterized, nearly atomic initial state. The initial-state effects are simple and the influence of the excited state on the cross section can be studied in detail. This influence depends on the geometrical properties of the system, and therefore cross-section measurements can yield structural information. This concept led very recently to a technique called photoelectron diffraction.

In a naïve picture, the wave function of the excited electron can be regarded as an outgoing spherical wave centered at the emitting atom—somewhat like the light emitted by a point source. These outgoing waves will be scattered in part by the atoms surrounding the emitting atom (*22*). A more realistic final-state wave function must then be a superposition of the outgoing spherical wave and of several different scattered waves.

Scattered-wave effects are quite dramatic in the photon energy dependence of the cross section. For an isolated atom the photoionization cross section of a particular core level is entirely determined by the atomic wave functions of the core level and of the excited state—and so is its dependence on the photon energy. For an atom in a solid the dependence of the cross section on photon energy retains some of its atomic character, as demonstrated by Lindau *et al.* (*23*). This dependence, however, is modulated by scattered-wave components of the excited state, which is no longer purely atomic. The effect on the cross section is somewhat similar to a diffraction or interference effect for visible light: the intensity observed in a particular direction decreases or increases as the wavelength is changed. In photoemission, the intensity corresponds to

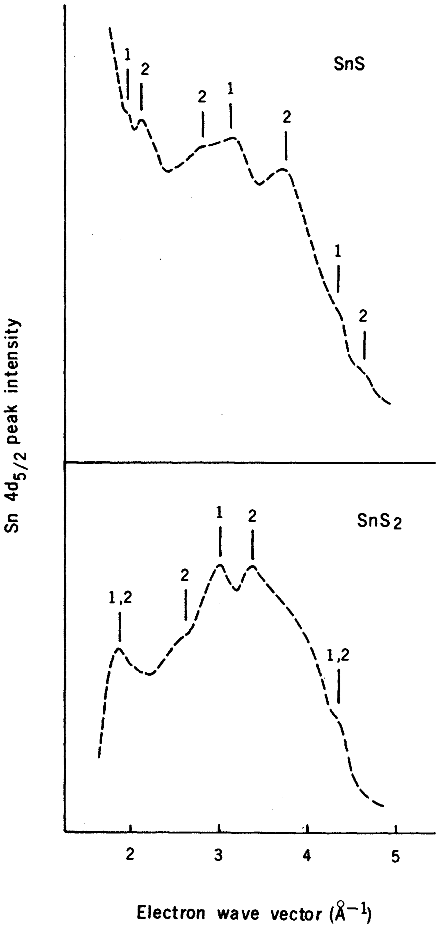


Fig. 8. Photoionization cross section of the Sn $4d_{5/2}$ core level in SnS and in SnS_2 (*24*). The cross sections are plotted as a function of the magnitude of the photoelectron wave vector, **k**. An increasing wave vector magnitude corresponds to an increasing kinetic energy, and this in turn corresponds to an increasing photon energy. A modulation is clearly visible in these curves and two series of peaks have been identified. The modulation is due to scattering of the outgoing photoelectron wave function back to the emitting atom by the surrounding atoms. For series 1 the backscattering atom is sulfur and for series 2 it is tin.

the number of emitted photoelectrons—that is, to the cross sections—and the wavelength of the electron is determined by its energy and hence by the photon energy.

In angle-integrated photoemission experiments, Margaritondo and Stoffel (*24*) recently showed that this cross-section modulation is due primarily to backscattering of the outgoing wave by neighboring atoms (see Fig. 8). Li and Tong (*25*) used photoelectron diffraction effects in angle-resolved photoemission for chemisorption geometry identification. Their calculated normal-emission cross sections are shown in Fig. 9 for selenium atoms on a nickel surface. The solid curve shows the corresponding experimental results of Shirley and co-workers (*26*). Best agreement between theory and experiment is found for a "hollow" chemisorption site, and this identifies the chemisorption geometry.

Another kind of photoelectron diffraction experiment based on scattered-wave effects is again suggested by the similarity between photoelectron diffraction and diffraction or interference effects for visible light. As for light, the intensity at a constant wavelength (that is, cross section at a constant kinetic energy) varies with direction and this gives rise to a diffraction pattern (*27, 28*). Effects of this kind have been detected by Woodruff *et al.* (*27*) for the core levels of tellurium and sodium chemisorbed on nickel. In their experiment the photoelectron collector was rotated around the sample normal so as to change the azimuthal angle. The radial plot of the azimuthal dependence of the photoemission intensity for the Na 2*p* core level on Ni(001) is shown in Fig. 10. The theoretical reproduction of these patterns leads to the identification of the chemisorption geometry.

Conclusions

The strength of the "new" photoelectron spectroscopy lies in its ability to study electrons in solids from many different points of view. For some electronic properties it is the best (and often the only) experimental probe. For example, it is the best way to measure the distribution in energy of empty and occupied electronic states. It is the only way to directly map electronic band structures. In other cases, the photoemission technique is complementary to other possible approaches—yet of fundamental importance because of its unique properties. Surface structures, for example, can be investigated by other techniques besides photoemission, such as low-energy electron diffraction. In contrast to electron diffraction, however, photoemission techniques can, in principle, be applied to systems without long-range order.

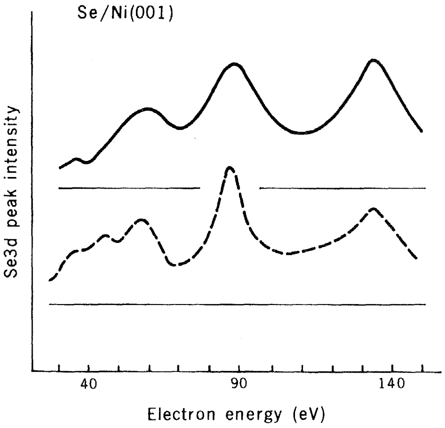


Fig. 9. Intense modulation has been observed by Shirley and co-workers (*26*) in the plots of the Se 3*d* cross section as a function of the photoelectron kinetic energy (solid line) for chemisorbed Se on Ni. The experimental curve has been theoretically reproduced (dashed line) by Li and Tong (*25*), using a "hollow" chemisorption site.

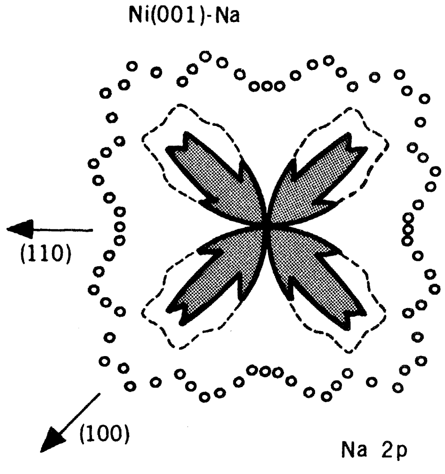


Fig. 10. Photoelectron diffraction effects modulate the azimuthal plots of the Na 2*p* core level photoemission intensity measured at a fixed polar angle (*27*). The dashed curve shows the experimentally measured pattern after correction for a constant background. The circles are calculated points and the shaded area corresponds to the same points after background subtraction.

Since the advent of stable synchrotron radiation sources in the late 1960's, photoelectron spectroscopy has rapidly evolved from a specialized probe of the density of occupied states into a multifaceted and very flexible technique. The "evolutionary" stage of photoemission with synchrotron radiation is nearing its end, and many of the new techniques utilizing it can be routinely applied to real and increasingly complicated systems.

References and Notes

1. For a detailed review of photoelectron spectroscopy see B. Feuerbacher, B. Fitton, R. F. Willis, *Photoemission and the Electronic Properties of Surfaces* (Wiley, New York, 1978); M. Cardona and L. Ley, *Photoemission in Solids* (Springer-Verlag, New York, 1978), vols. 1 and 2.
2. C. R. Brundle, *J. Vac. Sci. Technol.* **11**, 212 (1974).
3. R. Z. Bachrach, D. J. Chadi, A. Bianconi, abstract of paper presented at the 38th Conference on Physical Electronics, Oak Ridge, Tenn., 1978.
4. M. M. Traum, private communication.
5. D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **28**, 1327 (1972).
6. J. H. Weaver, D. T. Peterson, R. L. Benbow, *Phys. Rev. B* **20**, 4855 (1979); D. J. Peterman, B. N. Harmon, J. Marchiando, J. H. Weaver, *ibid.*, p. 4867.
7. G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, P. L. Gobby, *Solid State Commun.* **15**, 1601 (1974); G. J. Lapeyre, J. Anderson, P. L. Gobby, J. A. Knapp, *Phys. Rev. Lett.* **33**, 1290 (1974).
8. G. Margaritondo, J. E. Rowe, M. Schulter, A. H. Kasper, *Solid State Commun.* **22**, 753 (1977).
9. J. E. Rowe, G. Margaritondo, S. B. Christman, *Phys. Rev. B* **16**, 1581 (1977); M. Schluter, J. E. Rowe, G. Margaritondo, K. M. Ho, M. L. Cohen, *Phys. Rev. Lett.* **37**, 1632 (1976).
10. J. F. Janak, A. R. Williams, V. L. Moruzzi, *Phys. Rev. B* **11**, 1522 (1975).
11. N. V. Smith and M. M. Traum, *Phys. Rev. B* **11**, 2087 (1975).
12. D. R. Lloyd, C. M. Quinn, N. V. Richardson, P. M. Williams, *Commun. Phys.* **1**, 11 (1976).
13. P. K. Larsen, G. Margaritondo, J. E. Rowe, M. Schulter, N. V. Smith, *Phys. Lett. A* **58**, 523 (1976).
14. I. T. McGovern and R. H. Williams, *Nuovo Cimento B* **38**, 241 (1977).
15. Y. Petroff, in *Proceedings of the 13th International Conference on the Physics of Semiconductors*, F. Fumi, Ed. (Veschi, Rome, 1977), p. 975.
16. P. K. Larsen, N. V. Smith, M. Schulter, H. H. Farrell, K. M. Ho, M. L. Cohen, *Phys. Rev. B* **17**, 2612 (1978).
17. T. Grandke, L. Ley, M. Cardona, *Phys. Rev. Lett.* **38**, 1033 (1977).
18. J. A. Knapp, F. J. Himpsel, D. E. Eastman, *Surface Sci.*, in press.
19. E. Dietz and D. E. Eastman, *Phys. Rev. Lett.* **41**, 1674 (1978).
20. J. Hermanson, *Solid State Commun.* **22**, 9 (1977).
21. C. L. Allyn, T. Gustaffson, E. W. Plummer, *Chem. Phys. Lett.* **47**, 127 (1977).
22. A. Liebsch, *Phys. Rev. B* **13**, 544 (1976).
23. I. Lindau, P. Pianetta, W. E. Spicer, *Phys. Lett. A* **57**, 225 (1976).
24. G. Margaritondo and N. G. Stoffel, *Phys. Rev. Lett.* **42**, 1567 (1979).
25. C. H. Li and S. Y Tong, *ibid.*, p. 901.
26. S. D. Devan, D. H. Rosenblatt, D. Denley, B.-C. Lu, D. A. Shirley, *ibid.* **41**, 1565 (1978).
27. D. P. Woodruff, D. Norman, B. W. Holland, N. V. Smith, H. H. Farrell, M. M. Traum, *ibid.*, p. 1130.
28. S. Kono, C. S. Fadley, N. F. T. Hall, Z. Hussain, *ibid.*, p. 117.