100 YEARS OF PHOTOEMISSION

A century of scientific struggle has given us powerful photoemission spectroscopies for probing electronic structure and has brought us to the threshold of great advances based on new, high-brightness sources of synchroton radiation.

Giorgio Margaritondo

In a series of experiments on the effects of resonance between very rapid electric oscillations that I carried out and recently published, two electric sparks were produced by the same discharge of an induction coil, and therefore simultaneously. One of these, spark A, was the discharge spark of the induction coil, and served to excite the primary oscillation. The second, spark B, belonged to the induced or secondary oscillation. I occasionally enclosed spark B in a dark case so as to make observations more easily, and in so doing I observed that the maximum spark length became decidedly smaller inside the case than it was before.

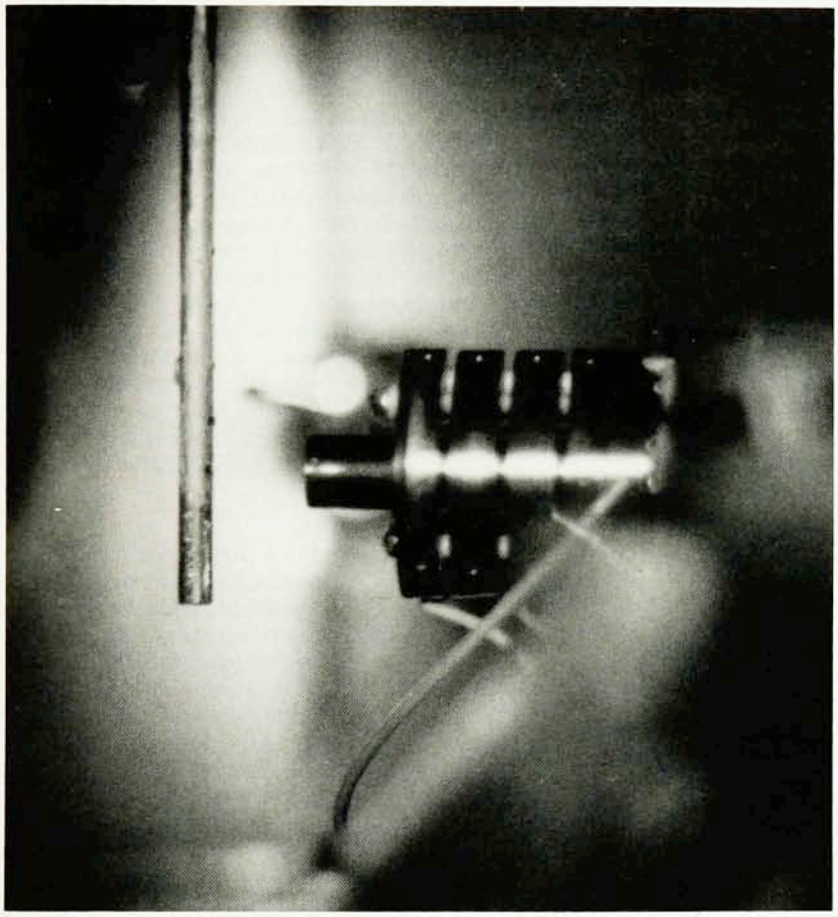
With these words, Heinrich Hertz announced in 1887 the discovery of the photoelectric effect.[1] Although he realized that the phenomenon was important, he certainly could not have imagined how fundamental its role in physics was to be over the next 100 years. Even now, many physicists do not completely understand that role. For example, the effect is often, but incorrectly, credited with leading Albert Einstein to the quantization of the electromagnetic field. Photoemission experiments actually made their most important contributions to field quantization *after* Einstein had formulated the theory, by demonstrating its validity.

The photoelectric effect is crucial to today's science and technology. Photoemission spectroscopy, for example, is one of the most advanced and productive areas of experimental physics, serving as a leading probe of the electronic structure of atoms, molecules, solids and solid interfaces. (See figure 1.) In this article I trace the development of photoemission techniques from Hertz's discovery to the present, when we stand at the threshold of further great advances stimulated by the advent of new, high-brightness sources of synchroton radiation. In reviewing this century of struggle with technical and conceptual problems, I concentrate on landmark results such as those of Hertz, Philipp Lenard, Einstein and Kai Siegbahn. I should emphasize, however, that these breakthroughs were made possible by a long series of contributions by scientists who are often forgotten. The centennial of the photoelectric effect is a good time to celebrate all the scientists, major and minor alike, who contributed to the development of modern photoemission.[2]

An accidental discovery

In 1879 the Berlin Academy of Sciences offered a prize for research "to establish experimentally any relation between electromagnetic forces and the dielectric polarization of insulators." Hermann Helmholtz called Hertz's attention to this problem, and stimulated him to initiate his historic experiments on the existence of James Clerk Maxwell's electromagnetic waves. Hertz performed these experiments at the Technische Hochschule in Karlsruhe, where he was a professor of experimental physics. His apparatus consisted basically of an oscillating circuit containing a spark gap, which generated the waves, and a second, suitably tuned circuit, which received them. Their reception was established by observation of a spark across a gap in the second circuit. As Hertz's words cited above

Giorgio Margaritondo is a professor of physics at the University of Wisconsin, Madison, and is associate director of the university's Synchrotron Radiation Center.



Photoelectron analyzer facing the first cleaved single crystal of the high-temperature superconductor $YBa_2Cu_3O_x$. The tiny specimen, grown by Patricia Morris and William Bonner, is mounted on the vertical rod, together with similar crystals. In this experiment at the Wisconsin Synchrotron Radiation Center, a Bellcore–Wisconsin team headed by Ned Stoffel, Marshall Onellion and the author probes the surface of the crystal using an angle-resolved photoelectron energy analyzer. Helen Farrell of Bellcore designed the photoemission system. **Figure 1**

indicate, the weakness of the induced spark prompted him to enclose the secondary spark gap in a dark case to make the observations easier. This, however, revealed an unexpected interaction between the two sparks. As we now know, the secondary spark was facilitated by the light-induced emission of electrons from the electrodes. The photoelectrons in the secondary spark gap were generated by ultraviolet photons emitted by the primary spark. The case absorbed the ultraviolet radiation, making it more difficult to produce the secondary spark.

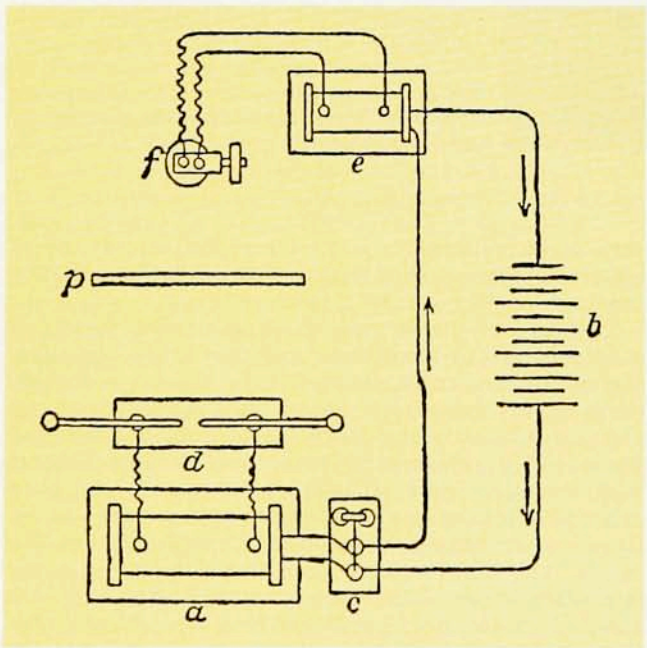
These events annoyed Hertz because they interfered with his main line of research: "I had no intention of allowing this phenomenon to distract my attention from the main object I had in view, but it occurred in such a definite and perplexing way that I could not altogether neglect it."[1] Eventually, his appreciation of the importance of the new phenomenon prevailed, and he interrupted his main experiments to study the effect in detail. Figure 2 illustrates the experimental system that produced the best results. Two sparks were generated at the gaps d and f by the Ruhmkorff coils a and e, which were powered by the same series of Bunsen cells, b, through the mercury circuit breaker c. Hertz studied the interference between the two sparks by placing a plate, p, between them.

Hertz used plates made of an impressive variety of materials: metals (both thick and thin sheets), paraffin, shellac, resin, ebonite, various kinds of glass, porcelain, earthenware, mica, agate, wood, pasteboard, paper and also, *ad abundantiam*, ivory, horn, animal hides and feathers. He performed his most significant experiments with crystals. Some of these, notably rock salt, had minimal effects on the interference between the sparks. Hertz's observations, corroborated by refraction experiments, led him to identify ultraviolet light as the immediate cause of the phenomenon: "After what has now been stated, it will be agreed that the light of the active spark must be regarded as the prime cause of the action. And if the observed phenomenon is an effect of light at all it must be solely an effect of the ultraviolet light."

Hertz's experiments could not identify electrons as the other main ingredient of the phenomenon. The

problem, of course, was that the electron itself had not yet been discovered. Soon after Hertz's announcement, it became clear that ultraviolet radiation caused the emission of negatively charged particles from solids. In 1888 Wilhelm Hallwachs found that a negatively charged, insulated zinc plate would lose its charge when exposed to ultraviolet radiation, while a neutral plate would become positively charged.[2] In 1897 J. J. Thomson announced the discovery of the electron, and within two years he had demonstrated that the negative particles emitted in the photoelectric effects were electrons: "The following paper contains an account of measurements of m/e and e for the negative electrification discharged by ultra-violet light. The value of m/e in the case of ultra-violet light is the same as for the cathode rays."[3]

Lenard obtained the same result independently,[4] using the apparatus shown in figure 3. This apparatus is a precursor of the modern electron analyzers used for photoemission spectroscopy. Ultraviolet radiation produced by a spark bombarded a cathode, U, in an evacuated glass tube. The cathode could be biased with an external dc voltage supply. The anode E consisted of a screen at ground potential, with a small hole. The electrodes α and β, which were connected to electrometers, detected photoelectrons passing through the hole in the anode. The trajectory of these electrons could be modified by inducing a magnetic field with a pair of Helmholtz coils, represented in the figure by the dotted circle. Without the field, electrode α detected the electrons. When the coils were operated, electrode β detected the electrons for certain combinations of cathode bias voltage and magnetic field strength. From these data, Lenard computed the electron charge-to-mass ratio e/m. By using various cathode bias voltages, he made another fundamental discovery: For each cathode there was a maximum value of the photoelectron kinetic energy. The intensity of the ultraviolet light did not affect this maximum kinetic energy, although it did determine the number of photoelectrons emitted per unit time. These results remained unexplained until Einstein's quantum theory of the photoelectric effect.



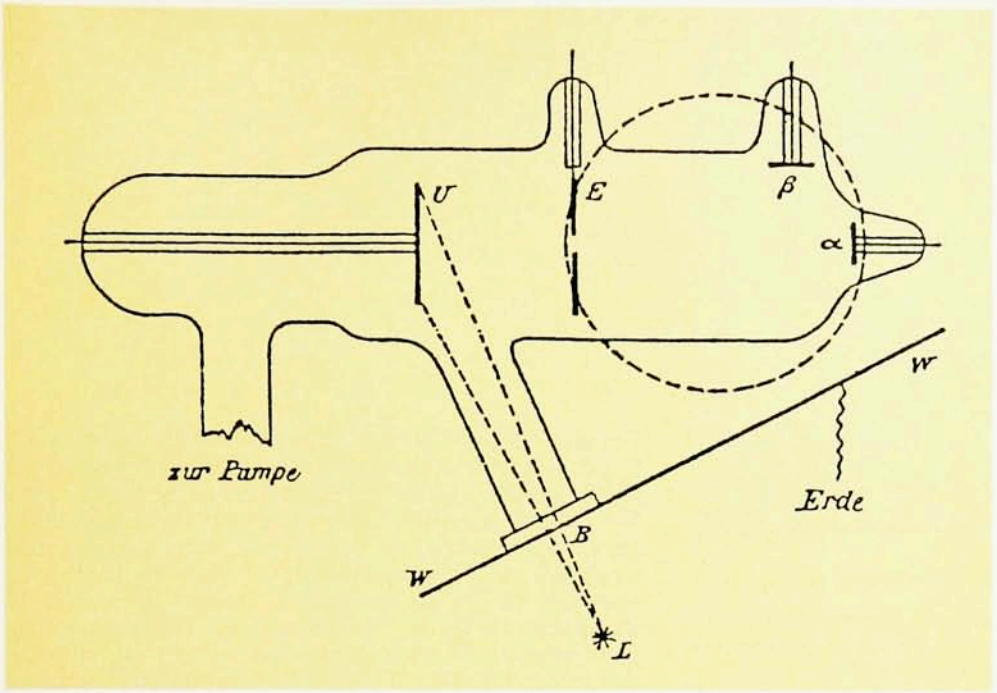
Schematic diagram of the experimental system that Heinrich Hertz used in 1887 to study the newly discovered photoelectric effect. (From H. Hertz, *Electric Waves*, McMillan, London, 1900.) Figure 2

Discovery of the photon

In 1905 Einstein published an article titled "On a Heuristic Point of View about the Creation and Conversion of Light," in which he suggests that electromagnetic energy is quantized.[5] This article includes the quantum theory of the photoelectric effect, for which Einstein received the Nobel Prize in 1921. A common misconception is that Einstein derived the concept of the photon from the results of experiments on the photoelectric effect. This would not have been possible with the data available in 1905, although Einstein acknowledged that Lenard's experiments on photoemission were one of his inspirations: "The production of cathode rays by ultraviolet light can be better understood on the assumption that the energy of light is distributed discontinuously in space." Einstein's derivation of the concept of photons was actually based entirely on statistical mechanics.

The revolutionary character of this derivation cannot be overestimated. At the time, the overwhelming evidence appeared to favor Maxwell's theory of the electromagnetic field. Lenard's results on the photoelectric effect seemed not to be a serious challenge to this theory. Five years earlier, Max Planck had rather unwillingly initiated the quantum revolution, but he had stopped short of questioning Maxwell's picture of the radiation inside his version of the blackbody. Against this formidable *status quo*, Einstein proposed a simple but powerful argument. He considered the entropy in a volume V_1 due to radiation in a frequency interval ν to $\nu + d\nu$. He assumed that Wilhelm Wien's radiation law is valid in the spectral region containing this interval, and demonstrated that the change in entropy caused by an isothermal change in volume from V_1 to V_2 is $(k_B\, dE/h\nu) \ln(V_1/V_2)$, where dE is the total energy of the radiation in the frequency interval ν to $\nu + d\nu$. This relation is equivalent to the expression for an ideal gas as long as the number of particles in the gas is $dE/h\nu$. Thus the radiation itself consists of "particles" of energy $h\nu$.

In the last part of the article, Einstein used this



Apparatus used by Philipp Lenard to demonstrate that the particles emitted in a photoelectric process are electrons. The instrument shown in this diagram is a precursor of modern photoelectron spectrometers. (From P. Lenard, *Ann. Phys. (Leipzig)* **2**, 359, 1900.) **Figure 3**

elegant result to formulate the quantum theory of the photoelectric effect. In this theory he predicted, based on the transfer of energy from photons to electrons, that the energy of the photoelectron would be $h\nu - P$, where P is "the amount of work that the electron must produce on leaving the body." For photoelectrons emitted with the maximum kinetic energy from a metal, P coincides with the work function. Einstein's linear frequency law was consistent with Lenard's results, but could not be tested with the data available in 1905. The first experiments on the frequency effects after 1905 produced somewhat ambiguous results. Some experimenters claimed that the maximum photoelectron velocity, rather than the maximum energy, depended linearly on the frequency. This incorrect conclusion was the product of insufficient and inaccurate data.

In 1912 the classic experiments by Arthur Llewelyn Hughes and by Owen Williams Richardson and Karl Taylor Compton clearly demonstrated the validity of Einstein's frequency law.[6] Figure 4 shows some of Hughes's data. Experiments in 1916 by Robert A. Millikan made the evidence in favor of Einstein's model complete.[7] These 1912 and 1916 experiments were the most important contributions of the photoelectric effect to the development of quantum physics. They definitively established the quantization of the electromagnetic field. Together with Niels Bohr's theory of the hydrogen atom, published in 1913, these results made irreversible the revolutionary process started by Planck.

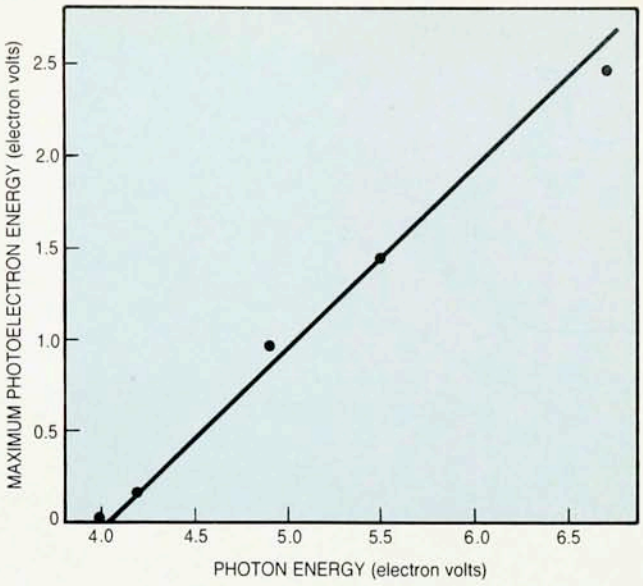
Photoemission spectroscopy evolves

In the late 1910s, three decades after the discovery of the photoelectric effect, conditions appeared to be good for the development of a new spectroscopy based on photoelectrons. A strong theory linked the energy distribution of photoelectrons to the ground state distribution of electrons in the emitting system. In 1914 H. Robinson and W. F. Rawlinson began using x-ray lines to excite photoelectrons, opening the way for detailed analysis of the energy distribution of photoelectrons.[8] However, two problems delayed the actual birth of modern photoemission spectroscopy by more than three decades: poor energy resolution and insufficient quality of photoemitting surfaces.

The resolution was determined by the bandwidth of the photon source and by the resolution of the electron analyzer. Robinson and Rawlinson's use of x-ray lines improved the photon resolution, but their pioneering experiments, as well as those of Maurice de Broglie[9] and others, were severely limited by poor analyzer resolution.

Surface quality dramatically affects photoelectric emission in solids because the excited electrons have a very short mean free path. In a typical experiment, the kinetic energy of the photoelectrons ranges from a few electron volts to a few hundred electron volts. At these energies, electrons can travel only a few angstroms or a few tens of angstroms inside the solid before being inelastically scattered. Thus only electrons that absorb photons in a region very close to the surface can travel to the surface, escape and become photoelectrons. This situation is complicated by surface contamination, which dramatically affects phenomena in the thin escape region.

Starting in the early 1900s several scientists explored the short "escape depth" for photoelectrons. In 1919 Compton and L. W. Ross treated the experimental and theoretical problems encountered in measuring the escape depth.[10] However, their work had severe deficiencies. For example, it did not find evidence that the mean free path depends on the electron energy. It did, however, clearly establish that the escape depth is on the order of angstroms or tens of angstroms. Unfortunately, this fundamental fact was largely ignored in subsequent decades, and surface contamination rendered most of the corresponding data almost useless. The problem was



Maximum kinetic energy of electrons dislodged from cadmium, as a function of photon energy. These experimental data, taken by Arthur L. Hughes in 1912, demonstrated the linear relation predicted by Albert Einstein's model.[6] **Figure 4**

solved completely only with the advent of commercial ultrahigh-vacuum systems capable of routinely delivering pressures of 10^{-10}–10^{-11} torr. At these pressures, a clean surface, prepared, for example, by cleaving a crystal, becomes contaminated only after several hours or days, giving one time to perform photoemission experiments on surfaces essentially free of contamination.

In the years between the two world wars, photoemission spectroscopy went into a deep depression as experimenters shifted their attention to the competing techniques of x-ray absorption spectroscopy and x-ray emission spectroscopy, which could achieve better resolution. Photoemission research did, however, produce fundamental results outside of spectroscopy. In 1923 Kenneth Kingdon and Irving Langmuir discovered that a cesium coating lowers the work functions of surfaces.[11] This result indirectly influenced the discovery of the first photocathode with a good quantum yield, the Ag–O–Cs photocathode.[12] The subsequent development of many kinds of efficient photocathodes had an important impact on optical research and technology. Another fundamental event of the 1920s was Arnold Sommerfeld's formulation of his theory of metals. In the context of this theory, the work function, which is the most fundamental parameter for the photoelectric effect, enters into several other phenomena such as thermionic emission and field emission.

Modern photoemission spectroscopy

In the 1950s and 1960s a series of experimental breakthroughs made photoemission spectroscopy a leading probe of the electronic structures of atoms, molecules and solids. The two branches of the field—x-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy—are quite different and evolved rather independently. In XPS the photons have enough energy to extract photoelectrons from deep, atomic-like core levels. In UPS the photoelectrons are extracted mainly from valence states.

The development of XPS was primarily the result of an extensive experimental program at the University of Uppsala, Sweden, by Kai Siegbahn and his coworkers.[13] This work, which produced a second Nobel Prize both for photoemission and for the Siegbahn family, began in the early 1950s. Siegbahn had considerable experience in the design and construction of high-resolution electron spectrometers for β-ray spectroscopy. When he turned his attention to the photoelectrons created by x rays he estimated that the new instruments could achieve resolutions competitive with those obtained in x-ray emission and absorption spectroscopy. His first attempts, however, were frustrated by sample contamination. In the late 1950s Siegbahn described the solution to this problem in a personal letter to John G. Jenkin, R. C. G. Leckey and J. Liesegang, physicists at La Trobe University in Bundoora, Australia: "I recall that my students on the project and I had been unable to record any photoelectron spectrum at all from any sources we tried for several months, in spite of the fact that the instrument was running very well for radioactive sources using ThB. We then late one night tried a newly split NaCl crystal and suddenly we recorded our first photoelectron spectrum with extremely sharp lines and with the expected intensities."[2]

The "extremely sharp lines" are produced by the excitation of electrons from the core levels of the atoms in the solid. They are clearly visible in figure 5, which shows a spectrum for sodium chloride recorded by Siegbahn's group several years after the initial success. One could use these lines to analyze the chemical composition of the specimen. Furthermore, in the early 1960s Siegbahn and his coworkers demonstrated that one can use the energy positions of the lines to extract detailed information on the chemical bonds of each atomic species. The charge distribution of the valence electrons involved in bonding modifies the core energy levels with respect to the free-atom values, and therefore modifies the kinetic energies of the corresponding photoelectrons. Measurements of these "chemical shifts," which were already known in x-ray absorption and emission spectroscopy, immediately became a primary goal of x-ray photoemission spectroscopy. The excellent signal levels produced by Siegbahn's instruments made it possible to extend XPS to molecules in the gas phase. Three decades of research, initiated by Siegbahn's work, have transformed XPS into an exceedingly sophisticated technique. Virtually all aspects of the core-level photoemission process have been analyzed and exploited to extract information, including a variety of many-body effects and differences due to chemical shifts between bulk and surface atoms in solids.

The birth of UPS, like that of XPS, was prompted in part by advances in instrumentation. Important examples are the development of high-intensity ultraviolet lamps such as the helium line source, the use of windowless capillary connections between source and sample, and the construction of high-resolution electron energy analyzers based on electrostatic deflection. Unlike

that of XPS, however, the development of UPS cannot be attributed to a single group. Early experiments revealed clear connections between the ultraviolet photoemission spectra and the band structures of solids. William Spicer's formulation of the three-step model provided a simple conceptual framework for the interpretation of the UPS curves.[14] This model divides the solid-state photoemission process into three independent steps: optical excitation, transport to the surface and emission into the vacuum. This approximation made it possible to analyze the many factors that affect the photoemission spectra, and emphasized the contribution of the ground state electronic structure, which dominates the first step. Similar work has established a clear connection between the ground state electronic structures of molecules in the gas phase and their UPS curves.

Several articles in PHYSICS TODAY have described the evolution of XPS and UPS in recent years.[15] Investigators can now control or scan virtually all the parameters relevant to a photoemission experiment: photon energy, direction and polarization; photoelectron energy, direction and spin polarization; and various characteristics of the sample. One gets better measurements as one controls and scans more variables—and this flexibility and effectiveness is itself the best measure of the status of modern XPS and UPS.

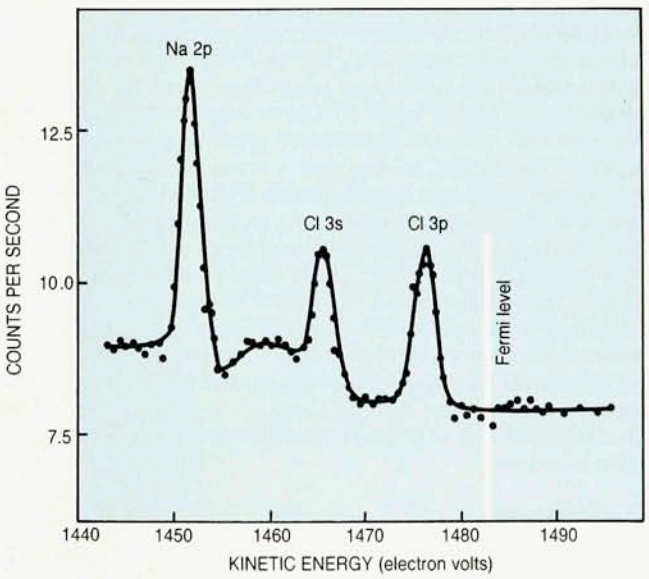
Spectacular advances in the quality of instrumentation over the past two decades are largely responsible for today's advanced state of photoemission spectroscopy. For example, the extensive use of efficient electron detectors such as the channeltron is crucial in modern angle-resolved photoemission experiments. The channel plate, an area-sensitive detector, has been used in sophisticated electrostatic analyzers that display the spatial distribution of the photoelectron intensity.

The major advance in instrumentation was the development of synchrotron radiation as a tunable, intense, polarized source of ultraviolet and x-ray photons. The complete control that synchrotron radiation gives the experimenter over the photon's parameters has had an impact on almost every area of photoemission spectroscopy. For example, by tuning the photon energy one can control the escape depth of the photoelectrons and distinguish between the contributions from bulk and surface electronic states. Experimenters studying surface chemical and physical phenomena such as corrosion, catalysis and the formation of interfaces make extensive use of this technique.[15] The intensity and brightness of synchrotron radiation are important when one studies the angular distribution of photoelectrons with small-area detection schemes. An example is the use of angle-resolved photoemission to measure the energies and **k** vectors of valence electrons in crystalline solids and to map their band structures. Figure 6 shows the results of an early application of this technique.[16] Modern XPS and UPS techniques go beyond the measurement of electron energies, the classic domain of photoemission, to explore the states of the electrons—that is, their wavefunctions—giving us a complete understanding of the electronic structure.

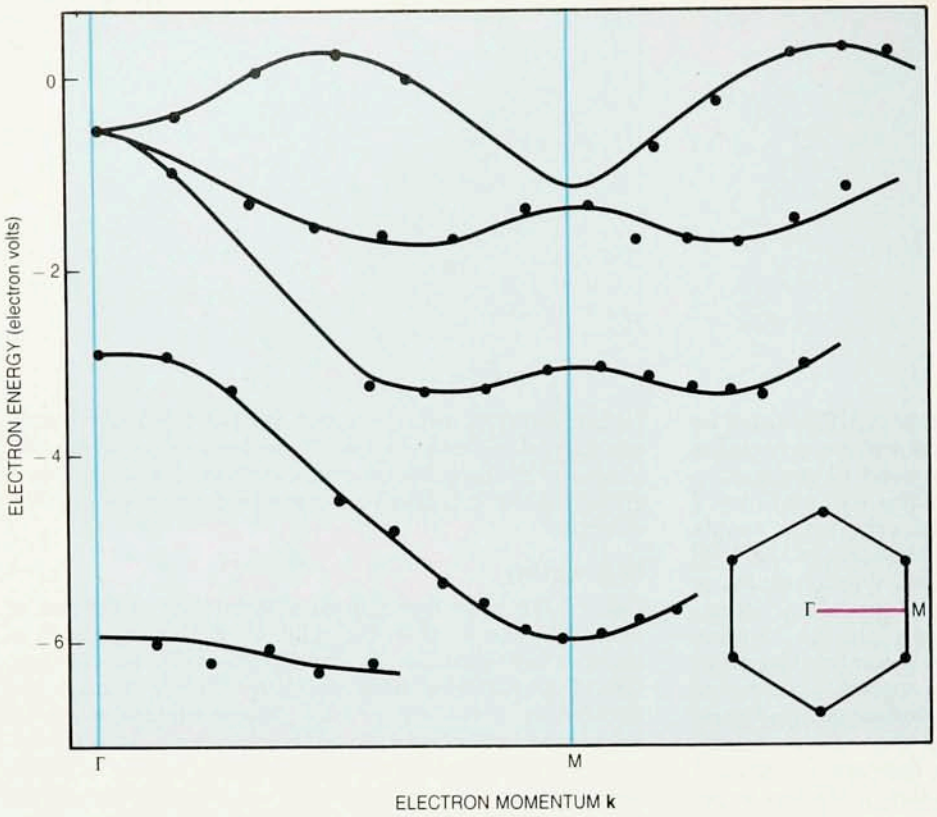
The future

One of the most amazing aspects of this centennial of photoemission is that the field is at the threshold of another rejuvenation. The construction of a new generation of synchrotron radiation sources based on magnetic undulators is now under way. These sources will have unprecedented intensities and brightnesses. The undulators at the Advanced Light Source at Berkeley and at the low-emittance ring at Trieste, for example, will be orders of magnitude brighter than sources at any existing soft-x-ray facility. These new sources will be a boon to those photoemission techniques that are now severely restricted by low signal levels. Furthermore, they will make possible novel photoemission experiments that are not feasible at present signal levels.

The study of the spin polarization of photoelectrons is one area of research that is now exceedingly difficult due to low signal levels. Measurements of the spin polarization of photoelectrons by Maurice Campagna and his coworkers at KFA (Jülich, West Germany) and by other



X-ray photoemission spectrum of sodium chloride recorded at the University of Uppsala by Kai Siegbahn and his coworkers. The spectrum exhibits sharp lines caused by the excitation of photoelectrons from atomic-like core levels. **Figure 5**



Band structure of gallium selenide as measured by angle-resolved photoemission. Since the mid-1970s, photoemission data have yielded plots of electron energy as a function of the **k** vector. This figure shows one of the first such plots, obtained in 1976 by Bell Laboratories scientists at the Wisconsin Synchrotron Radiation Center. The band structure is mapped for the Γ–M direction in the Brillouin zone, as shown in the inset.[16] **Figure 6**

groups have already yielded fundamental information on the magnetic properties of solids.

Photoemission microscopy and experiments resolved in time are just two novel photoemission techniques that stand to benefit from the new sources. Past attempts to implement photoemission microscopy had to trade off energy resolution against space resolution. The new sources will make it possible to achieve good space and energy resolution at the same time. Instrumentation based on multilayer coatings with high reflectivities for x rays will have energy resolutions on the order of a tenth of an electron volt and spatial resolutions on the order of a few hundred angstroms. These instruments will produce micrographs that show the chemical situation of each element in a specimen—information that is of crucial importance in molecular biology, microelectronics and other areas. The excitement generated by these research opportunities is the best celebration of Hertz's discovery, and the best way to begin the second century of photoemission research.

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