Photoelectron Spectroscopy of α- and δ-Plutonium

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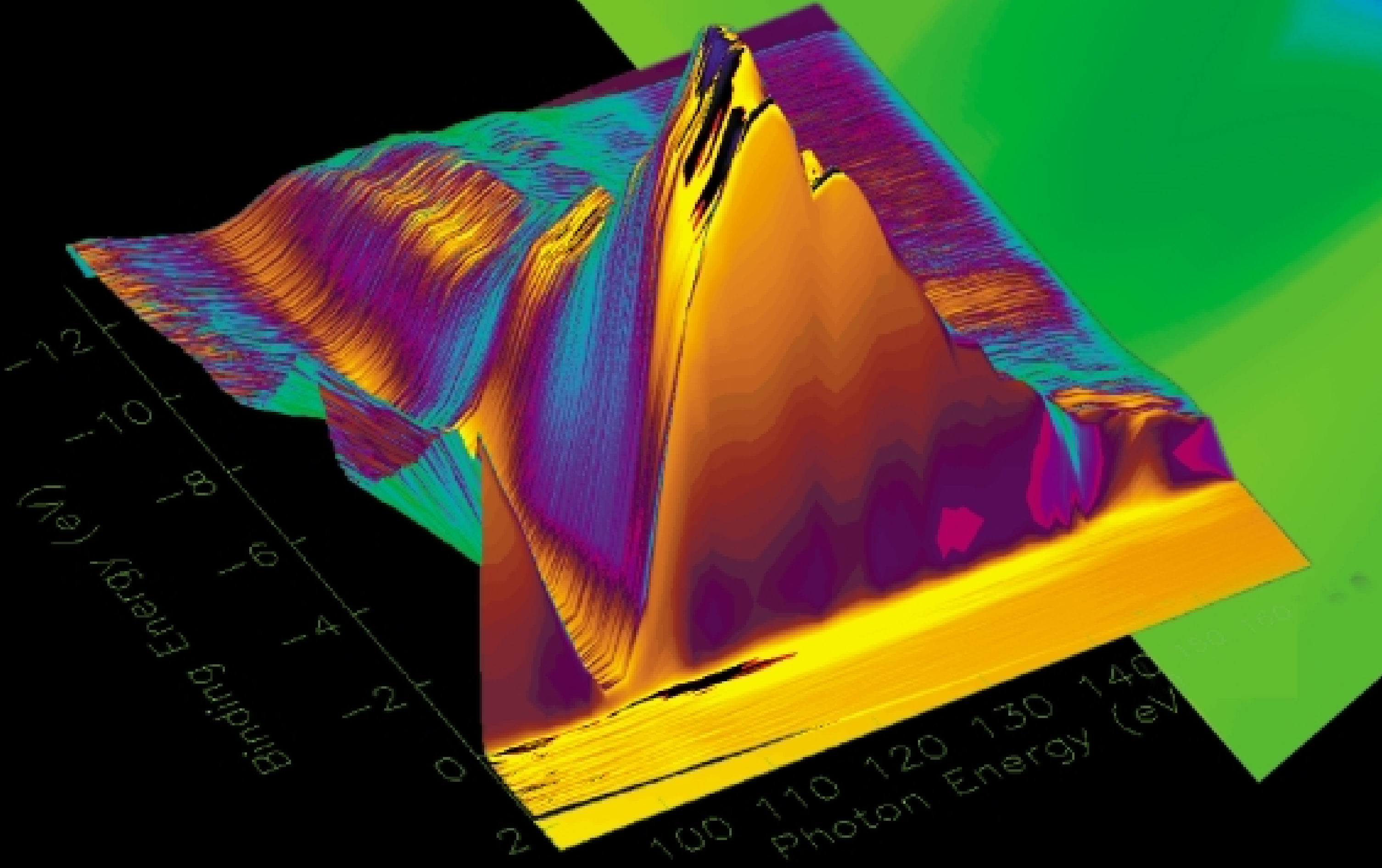

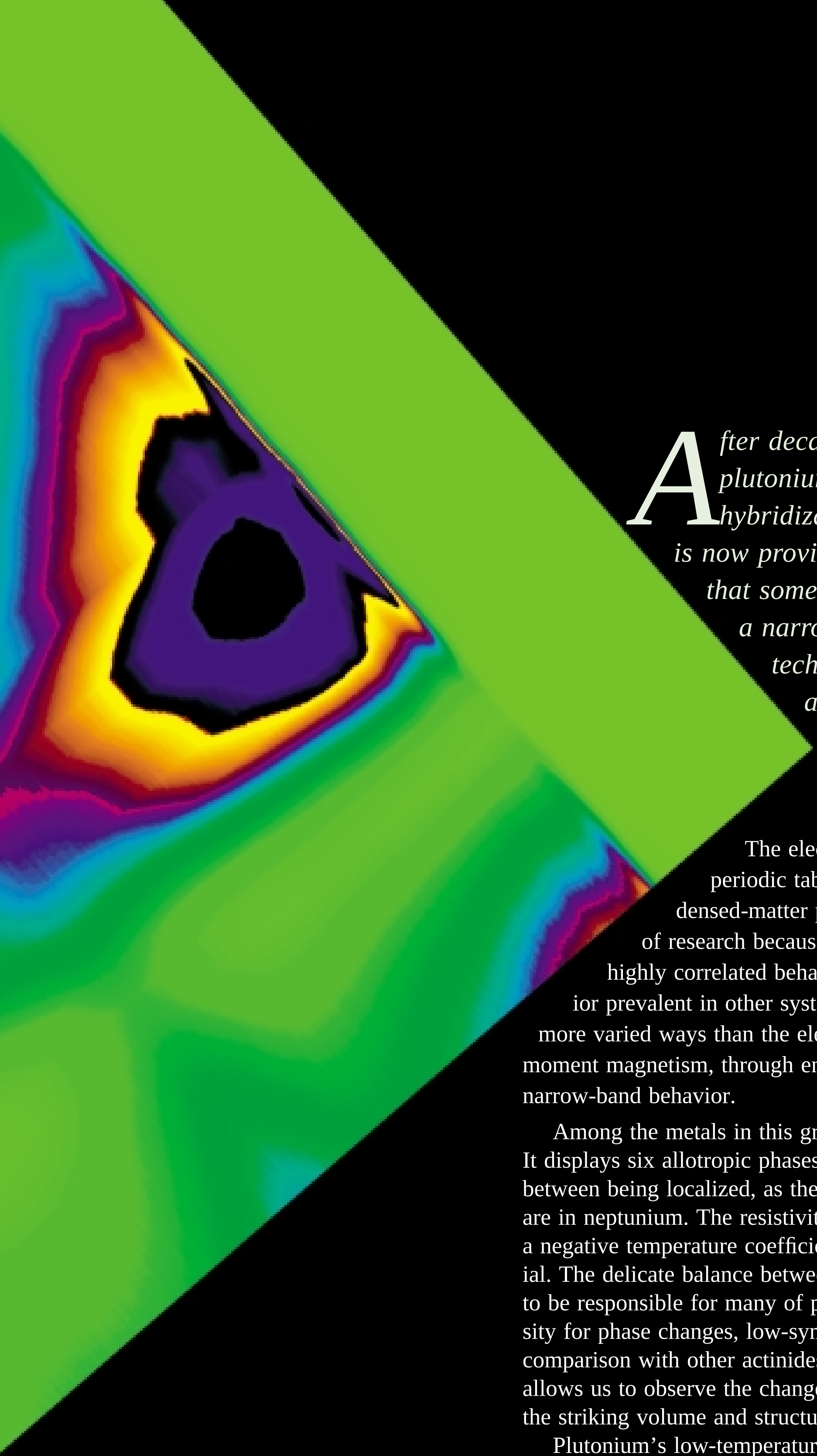

After decades of speculation about the role of plutonium's 5f electrons in bonding and hybridization, photoelectron spectroscopy (PES) is now providing the first detailed results indicating that some of the 5f electrons are itinerant and form a narrow conduction band. This measurement technique probes electronic structure directly and with great accuracy, defining a new path into the complex world of actinide behavior.

The electronic structure of the 5f series of metals in the periodic table represents a relatively unexplored area in condensed-matter physics. It is also one of the most interesting areas of research because the 5f electrons in all these elements tend toward highly correlated behavior as opposed to the independent-particle behavior prevalent in other systems. The 5f electrons in the actinides behave in more varied ways than the electrons in any other series of elements—from local-moment magnetism, through enhanced specific heat like heavy fermions, to narrow-band behavior.

Among the metals in this group, plutonium appears to be the most exotic. It displays six allotropic phases, and its 5f electrons are at the transition point between being localized, as they are in americium, and being delocalized, as they are in neptunium. The resistivities of both α- and δ-plutonium are large and have a negative temperature coefficient, which is highly unusual for an elemental material. The delicate balance between 5f electron bonding and localization is thought to be responsible for many of plutonium's unusual properties, including its propensity for phase changes, low-symmetry crystal structures, and low melting point by comparison with other actinides. Because of its many allotropic forms, plutonium allows us to observe the changes in electronic structure and their relationship to the striking volume and structural differences of those allotropes.

Plutonium's low-temperature phase (α-phase) has a simple monoclinic crystal structure and a high density—about 19 grams per cubic centimeter (g/cm^3). Typically, local-density approximation (LDA) band calculations suggest that the f-electron wave functions have direct overlap, yielding narrow but robust 5f bands. As a result, α-plutonium can be described as having transition-metal properties (see the article "Actinide Ground-State Properties" on page 128). By contrast, the high-temperature δ-phase is an fcc structure with a density of 16 g/cm^3. Direct f-f overlap is considered unlikely for most of the 5f electrons. Small residual hybridization with s and d band electrons, as proposed by the Periodic Anderson

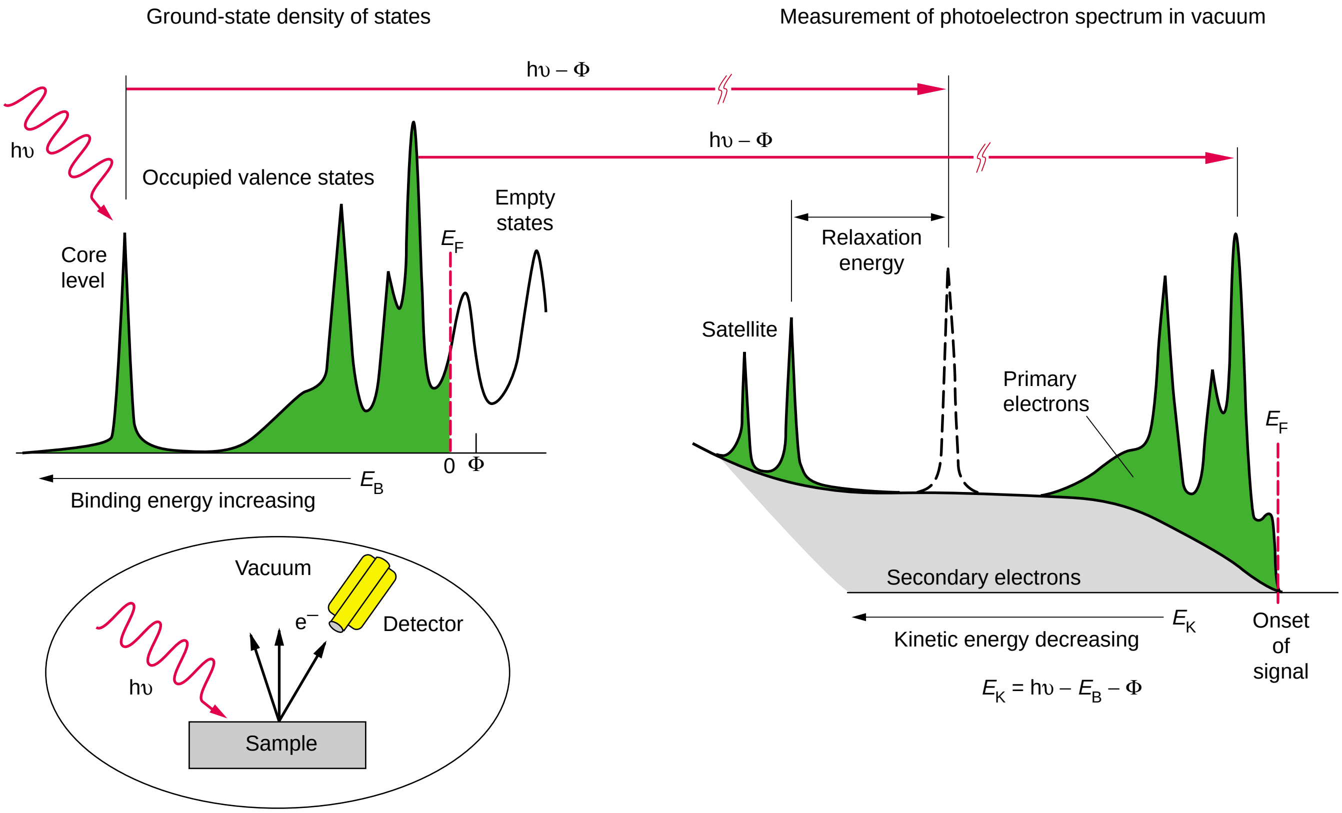

Figure 1. Schematic Representation of the Photoemission Process

The experimental setup for photoemission is shown in the inset at lower left. Monochromatic ultraviolet or soft x-ray light of energy hν is focused onto a clean sample surface in high vacuum (typically, 10^{-10} torr), and a detector records the number of photoelectrons emitted from the surface as a function of their kinetic energy E_K. The ground-state electronic structure is shown by the schematic density of states on the upper left. The filled states are shown in green and labeled by E_B, where the binding energy E_B is defined to be positive. The higher the binding energy E_B, the farther is the electron below the Fermi level at $E_B = 0$. Empty states above the Fermi level are not colored. Electrons at E_B absorb a photon of energy hν and are raised in energy by that same amount. If they are emitted into the vacuum, they lose not only the energy E_B needed to raise them to the Fermi level, but also the energy associated with the work function Φ due to an image charge at the surface. Thus, their kinetic energy in the vacuum is $E_K = h\nu - E_B - \Phi$, as shown on the right. The primary electrons are those at each E_K (this is what the spectrometer actually measures) transmitted into the vacuum without a scattering event. Their number is, to a first approximation, directly related to the number of electrons in the states E_B. Those electrons that are inelastically scattered before emission through the surface are called secondary electrons and contribute to a featureless background (indicated in gray). A core-level electron at ground-state energy E_{BC} may be emitted with energy $E_K = h\nu - E_{BC} - \Phi$ and produces the sharp dashed peak, provided the core hole left by the electron is well screened by the conduction electrons. Emission of core-level electrons may also lead to one or more satellites at lower E_K if the screening of the core hole is poor.

Model, or perhaps itinerancy from some fraction of the 5f electrons may yield some 5f density of states at the Fermi energy (see the articles "A Possible Model for δ-Plutonium" and "Actinide Ground-State Properties" on pages 154 and 128, respectively). Indeed, both resistivity data and recent magnetic-susceptibility measurements suggest that δ-plutonium has a narrow (very flat) conduction band pinned to the Fermi energy. Moreover, low-temperature specific-heat measurements indicate that the crystalline effective mass of conduction electrons at the Fermi energy is many times the rest mass of electrons, a property suggestive of heavy-fermion materials. Clearly, a detailed understanding of the plutonium 5f electronic structure is fundamentally important to the overall understanding of plutonium properties and to condensed matter physics as a whole.

In this article, we present measurements of the electronic structure of plutonium metal done by photoemission spectroscopy. Both α- and δ-plutonium were examined with several methods of surface preparation and in two independent photoelectron-spectrometer systems. The qualitative agreement between the two measurements is good. Spectra from both phases display a narrow 5f-related feature at the Fermi energy. That feature is narrower in δ- than in α-plutonium—a full width at half maximum (FWHM) of about 70 milli-electron-volts (meV) vs one of about 150 meV. The 70-meV FWHM is also typical of f electron peaks near the Fermi energy in heavy fermions. In both plutonium allotropes, the photon energy dependence of this feature suggests nonnegligible 6d admixture—albeit, somewhat less in δ-plutonium. These results were made possible by the design, development, and implementation of a unique laser-plasma light source at Los Alamos (by Arko, Joyce, and Morales) and by the first use of a synchrotron source to acquire photoemission data on plutonium metal (Terry and Schulze).

Basics of Photoelectron Spectroscopy (PES)

PES may be the most direct and detailed tool for measuring the electronic structure of metals. Photons of known energy (ultraviolet to soft x-ray) incident on a sample surface in vacuum are absorbed by the metal's electrons. The kinetic energy of these electrons increases by the amount of the photon energy. Electrons that are near the sample surface and that, prior to absorption, have a momentum component perpendicular to the surface[1] may escape from the material into the vacuum, where a detector records the number of electrons collected as a function of kinetic energy. As shown in the Figure 1 schematic, the measured photoelectron spectrum gives, to a first approximation, the shape of the occupied electron density of states in the sample (scaled by the orbital cross sections).

PES is especially effective when the photon source is tunable. We can then measure the photoelectron spectra at different incoming photon energies. Because the cross section for photoabsorption varies strongly with electron orbital symmetry at vacuum-ultraviolet (VUV) energies (Yeh and Lindau 1985), comparison of the different spectra at different photon energies allows identifying those spectral features that are due to electrons of a given orbital symmetry (s, p, d, or f). We can therefore compare such contributions as those of plutonium's 5f and 6d electrons.

In the very near future, when high-quality crystals with mirror surfaces become available, one could utilize precise sample-orientation devices to determine accurately the incoming photon direction, as well as the direction of the exiting electrons with respect to the sample surface. This angle-resolved PES technique, or ARPES, would allow development of a complete map of the energy bands—electron energies as a function of crystal momentum. Certainly, the latter possibility represents the future for research into the electronic structure of plutonium. Below, however, we limit the discussion to the simpler angle-integrated PES.

The PES Spectrum. Figure 1 defines the essential parameters of PES. Monochromatic ultraviolet or soft x-ray light of energy hν is focused onto a clean sample surface in high vacuum (typically, 10^{-10} torr). The electron energy in the material is specified by E_B, the binding energy, which is measured relative to the Fermi level, E_F. When an electron in the material absorbs a photon (the process may be described by dipole selection rules), its energy is raised by an amount hν. To escape the surface into the vacuum, the electron must have a momentum component normal to the sample surface, it must originate close enough to the surface—at the most, a few electron mean free paths (MFPs)—so that it should not be easily scattered, and it must gain sufficient energy from the photon in the normal component of momentum to overcome the electric dipole energy of the surface (usually referred to as the work function, or Φ). Once this photoelectron is in the vacuum chamber, its energy and momentum can be determined by an electron energy analyzer.

Because energy and, to some degree, momentum are conserved in the transmission through the surface, there is a simple relationship between the photoelectron's kinetic energy, E_K, in the vacuum and its binding energy, E_B, in the sample: $E_K = h\nu - E_B - \Phi$. (Actually, Φ is the work function of the analyzer because the measured kinetic energy of the electron is relative to the level of vacuum in the analyzer.)
To measure a typical spectrum, we count the electrons detected at any given kinetic energy in the vacuum, and the number detected is directly related to the number (density) of electrons within a given energy interval in the sample.

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[1] Note that photoabsorption does not alter the electron momentum significantly.

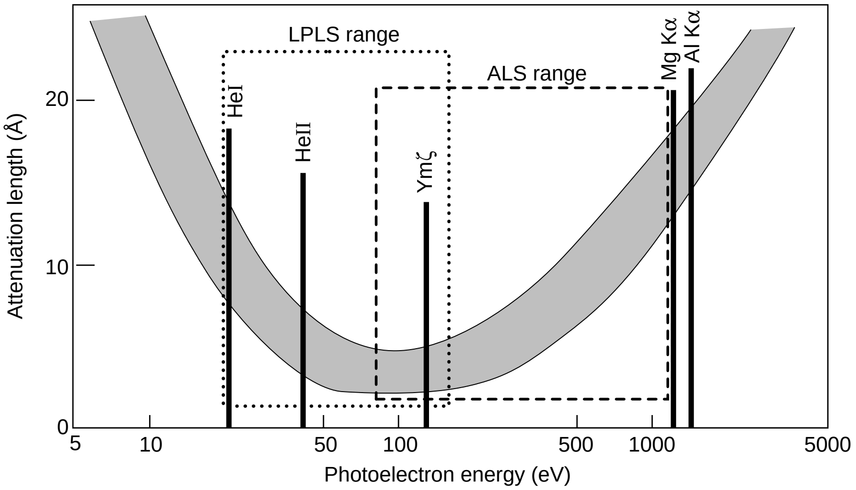

Figure 2. Universal Curve of the Probing Depth of PES

The photon energy range of the laser-plasma light source (LPLS) system is depicted by the dotted rectangle. The range of Beamline 7.0.1 at the Advanced Light Source (ALS) is shown by the dashed rectangle. Also shown are the energies of various line sources commonly used in PES. The attenuation length, or probing depth, is plotted as a function of the photoelectron energy. The probing depth is proportional to the MFP of the photoelectron, which has not yet exited the sample. Approximately 95% of the photoelectrons come from a probe depth within 3 MFPs of the surface.

The schematic view in Figure 1, however, greatly simplifies the true situation. In reality, many complications prevent the PES spectrum at a certain photon energy from being a replica of the occupied density of states, or the electronic band structure. Here, we consider two major complications: surface sensitivity and photoabsorption cross-section dependence on photon energy.

Surface Sensitivity. One limitation of PES is that it probes only the first few atomic layers of a material's surface. Although the surface and bulk electronic structures may differ, it has often been demonstrated that the bulk electronic structure of homogeneous solids is already well established at one or two monolayers below the surface. The universal curve in Figure 2 shows that the probing depth (related to the MFP of the outgoing electron) varies strongly with the kinetic energy of the outgoing electron, and the deepest probe (the greatest bulk sensitivity) occurs at very low and again at very high kinetic energies. This continuous variation allows us to separate surface from bulk features. We can measure a set of PES spectra at photon energies spanning a significant portion of the electron kinetic-energy range and then, by comparing them directly, distinguish surface from bulk features.

The great sensitivity to the surface layer also implies that atomically clean surfaces prepared in vacuum are an absolute requirement if one is to measure true bulk properties.

Photoelectron Cross Sections. As Yeh and Lindau point out (1985), the probability of an electron absorbing a photon—that is, the photoelectron cross section—varies strongly with the incident photon energy (hν), the electronic orbital symmetry (s, p, d, or f), and the atomic configuration (for example, *Z*-number and occupied energy levels). These variations complicate interpretation of the measured PES spectra and of the material's electronic structure. To obtain a complete picture of the density of states, one needs to take many spectra, using different photon energies, and then take into account the effects of the photoabsorption cross sections on the measured intensities of the photoelectron features.

Figure 3 shows photoabsorption cross sections for a plutonium atom calculated with the code of Yeh and Lindau (1985). At low photon energies—1 to about 30 electron-volts (eV)—the 6d states have the highest cross section and dominate the photoemission spectrum, whereas above about hν = 40 eV, the 5f states begin to dominate. In principle, one can therefore easily separate the 5f from the 6d contributions to the density of states by comparing several photoemission spectra taken at different energies in the range of 20 to 50 eV. Figure 4 shows such a set of spectra for the compound neptunium-arsenide (NpAs). The 6d emission predominates in the 21-eV spectrum. In Figure 4, we have overlaid copies of the 21-eV spectrum on the spectra taken at higher photon energies. Clearly, the 5f contribution grows dramatically with hν and may be deconvolved from the 6d features. Such a separation is possible for plutonium and any of its compounds or alloys.

Resonant PES. Another method to identify specific orbital contributions to the spectrum is resonant PES (Fano 1961). In this technique (see Figure 5), one works at a photon energy near the 5d absorption edge (approximately 115 eV for plutonium) to promote a 5d core-level electron into an empty 5f state just above the Fermi energy. Because this is primarily an atomic process, it is the final-state electronic configuration 5d^{9}5f^{n+1} that determines the exact photon energy (energies) at which resonance occurs (Lynch and Weaver 1987). As this electron decays to refill the core hole, it gives up its excess energy via an Auger-like process to a 5f (or, to a lesser extent, a 6d) electron near the Fermi energy. That

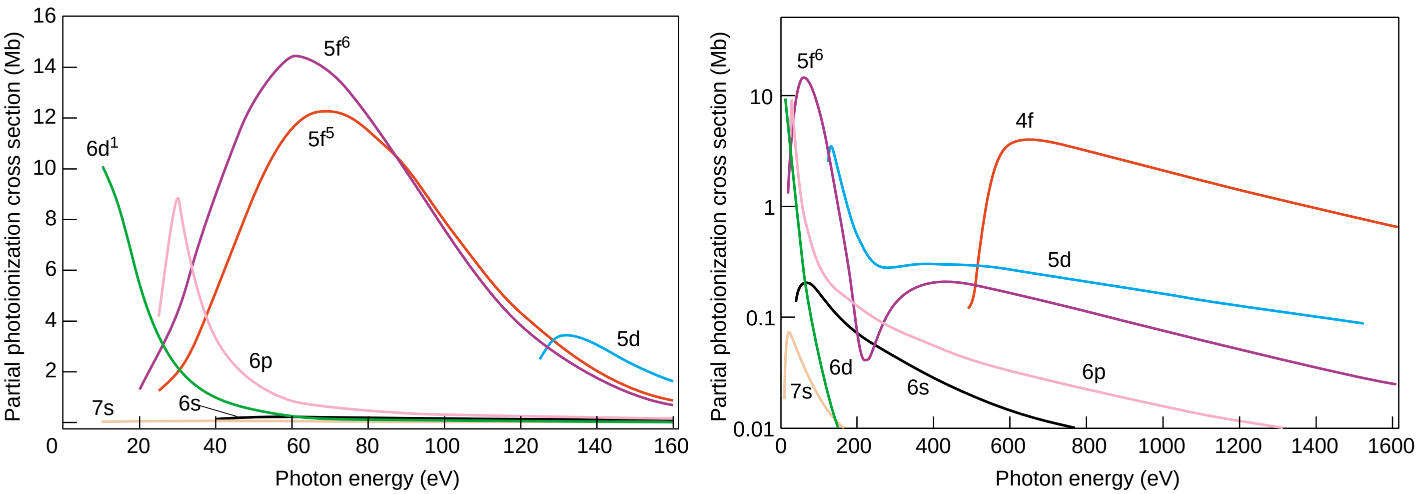

Figure 3. Calculated Photoabsorption Cross Sections for Plutonium

The photoabsorption cross sections for different atomic states in plutonium calculated using the methodology of Yeh and Lindau (1985) are shown here as representative of the cross sections in plutonium. (a) At low photon energies, the 6d cross section dominates over the 5f, but above approximately 30 eV, the opposite is true. The cross sections for the $5f^5 6d^1$ configurations are shown because they are more relevant to plutonium metal than the $5f^6 6d^0$ configuration of isolated atoms. (b) The cross sections for plutonium valence and core-level electrons down to the 4f state are plotted on a log scale up to 1600 eV.

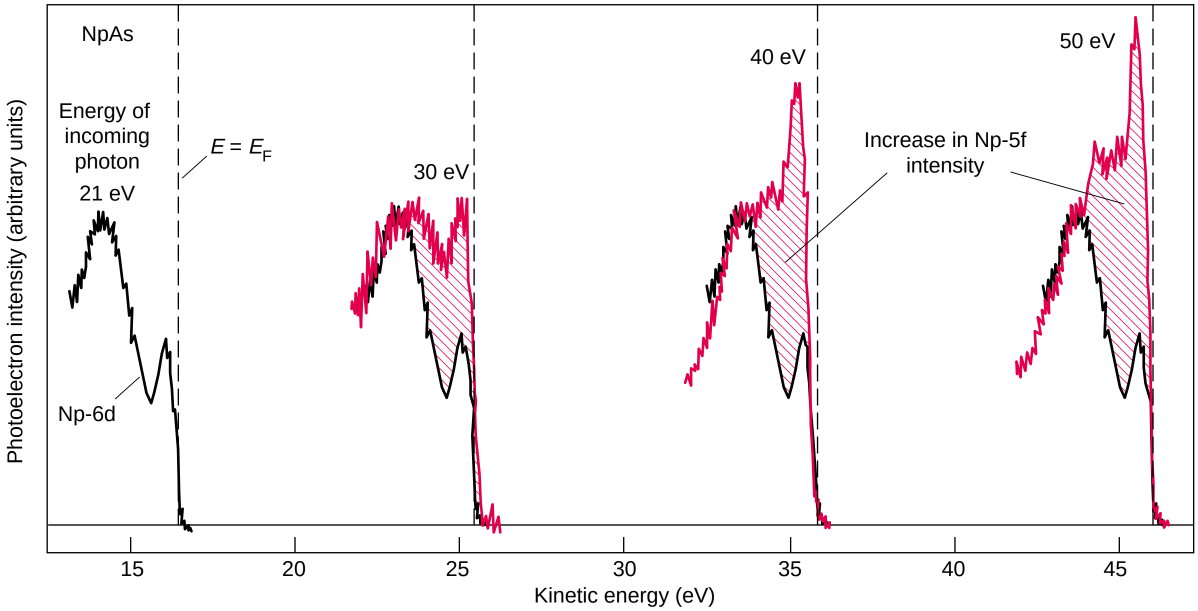

Figure 4. Photoemission Spectra of NpAs for Different Photon Energies

This plot shows several measurements of the d- and f-electron photoemission peaks as a function of photoelectron kinetic energy E_K. Because E_K increases with the incoming photon energy hν, the Fermi edges of the different spectra, indicated by the sharp and sudden onset of emission, are offset from each other by hν. The spectrum taken with hν = 21 eV, the lowest photon energy, has been superimposed on the spectra taken at higher photon energies. In each spectrum, the broad feature at –3 eV relative to the Fermi edge is due to the 6d electrons. The sharp peak at –0.5 eV relative to the Fermi edge increases in intensity as the photon energy increases. This increase, as well as the change in line shape, is due to increased 5f cross section and subsequent emission at higher hν. The increase in 5f intensity is represented by the hatched areas.

electron is ejected into the continuum of states above the vacuum level. (The refilling of the hole may produce a photon of commensurate energy instead of an Auger-electron, but the radiative process is much less favored.)

The Auger-like process yields a final state that is identical to that resulting from normal PES and therefore interferes either constructively or destructively with the normal PES photoabsorption. Because the resonant cross section (constructive interference) is very large (it is proportional to the cross section for the initial core-level process promoting a 5d electron into a 5f state), it greatly increases the 5f emission intensity in a narrow range of photon energies near the absorption edge. By contrast, destructive interference, or antiresonance, may yield almost zero 5f emission at the so-called antiresonance (approximately 104 eV for plutonium). Spectra of actinide compounds taken at resonance and antiresonance are particularly useful for separating the 5f and, to some extent, the 6d components from other electronic states.

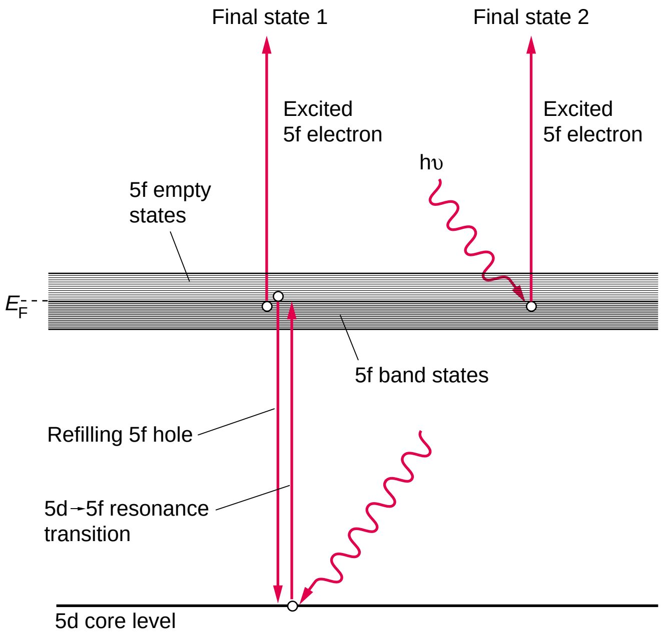

Figure 5. Schematic of Resonant Photoemission

In resonant photoemission in plutonium, a photon of energy hν is sufficient to promote a core 5d electron into an empty state, just above the Fermi level. As this electron decays to refill the core hole, it gives up its energy to a 5f electron in the occupied states via an Auger process, and the resulting state is final state 1. However, the identical final state can also be reached by direct photoemission and is depicted as final state 2. The two final states can interfere with each other constructively (resonance) or destructively (antiresonance). In plutonium, the resonance and antiresonance are at 120 eV and 104 eV, respectively.

Experimental Details

Powerful synchrotrons have been developed into intense tunable light sources for photoemission studies. The Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory represents the cutting edge of today's machines. Although potential hazards and political sensitivity surrounding plutonium have often precluded studying this material at synchrotron sources, the situation is being remedied, and as we will describe, Schulze and Terry have performed successful PES measurements of plutonium at the ALS. Arko and Joyce, on the other hand, designed, constructed, and currently operate a one-of-a-kind tunable laser-plasma light source (LPLS)[2], which mimics the output of a synchrotron. In addition, the LPLS system has an in situ capability for automatically producing clean actinide surfaces, an essential feature for work at VUV photon energies. The LPLS and ALS are described in the short articles "Laser-Plasma Light Source" and "Actinide Photoemission Measurements at the Advanced Light Source" on pages 186 and 188.

Surface preparation is crucial to a PES experiment because, as shown in Figure 2, the probing depth of PES is only a few atomic layers (in most metals, about 1 to 5 atomic layers, or 5 to 25 angstroms). Atomically clean surfaces are thus essential to accurate PES results. In the synchrotron experiments, surfaces are cleaned by sputter anneal, and in the LPLS experiments, by laser ablation—the laser beam is redirected into the vacuum chamber and cleans the sample. The latter technique is simple to use and allows cleaning the sample at low temperatures. Low temperatures are significant because they limit diffusion and reduce degradation reactions at the sample surface.

Figure 6 shows a sequence of PES spectra taken at five stages of in situ cleaning. The top spectrum is of the α-plutonium sample with a thick oxide overlayer, and it shows a broad oxide peak centered around an electron kinetic energy of 29 eV (E_B = –6 eV), which is due to the electrons in the oxygen 2p band states, and a second peak centered at 33.5 eV, which is due to the localized 5f electrons in the plutonium oxide. These LPLS data were taken at a photon energy of 40 eV to enhance the

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[2] Since 1992, this project has been funded by the Office of Basic Energy Sciences, Division of Materials Sciences, of the Department of Energy.

PES intensity of the oxygen 2p electrons relative to that of the 5f electrons. We used only a few laser pulses to ablate the sample surface between taking each of the subsequent spectra. Note that, with each cleaning, the Fermi edge grows in intensity whereas the oxide peak at a binding energy of –6 eV decreases and changes in shape (residual surface oxygen is still present in cycle 5, but by comparison with the starting oxide, it is clearly different in shape and reduced in intensity). The final metallic spectrum is dramatically different from the starting spectrum, but it is similar to the final spectra obtained by the more-traditional sputter-anneal (or scraping) methods, thus demonstrating the effectiveness of laser ablation.

In preparation for the synchrotron experiments at the ALS, the samples were first passed through numerous sputter-anneal cycles in the Chemistry and Metallurgy Research (CMR) Facility at Los Alamos, and they were examined by traditional x-ray photoemission and Auger surface spectroscopies. The samples were then transferred under vacuum into vessels maintained at a pressure of 10^{-8} torr by a portable battery-powered ion pump system. Being isolated from oxygen and air in these vessels, the samples were shipped to the Lawrence Berkeley National Laboratory, where they were transferred under vacuum to a preparation system appended to the x-ray photoelectron-diffraction analysis chamber of the Spectromicroscopy Facility Beamline 7.0.1 (see the article "Actinide Photoemission Measurements at the Advanced Light Source" on page 188). In the preparation chamber, the samples underwent final sputter-anneal cleaning cycles before being transferred into the chamber for synchrotron PES measurements.

Using these techniques, we have obtained the world's first resonant-photoemission data on α- and δ-plutonium. The higher resolutions and cleaner surfaces made possible by laser ablation have yielded dramatic,

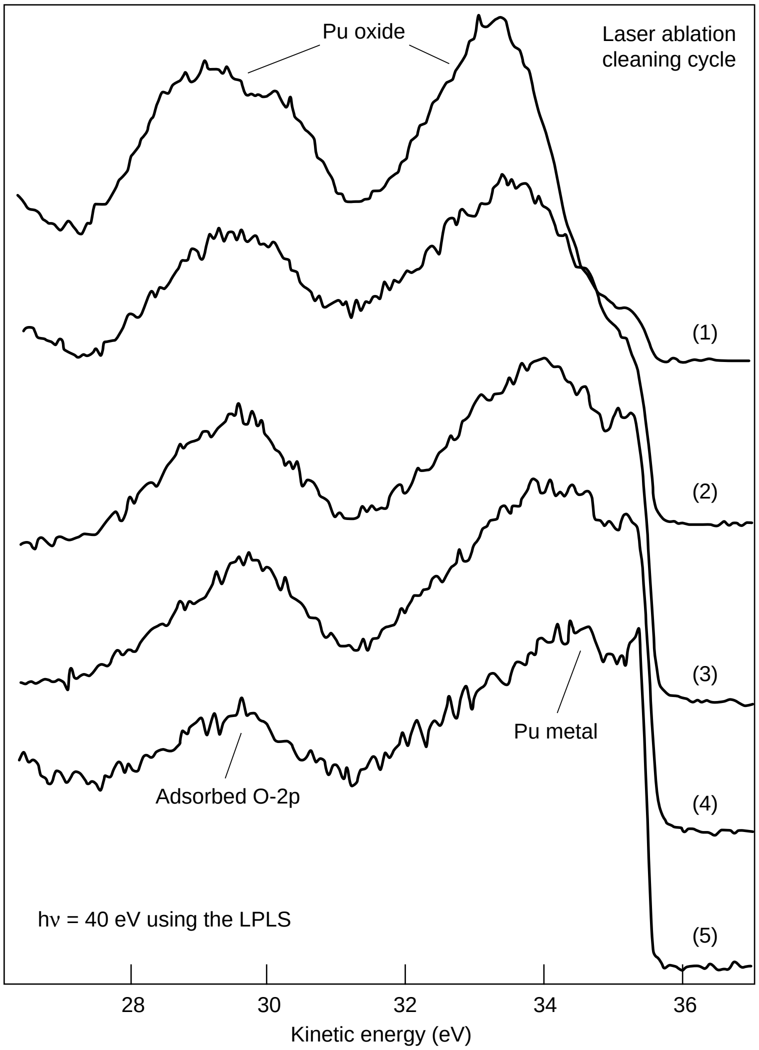
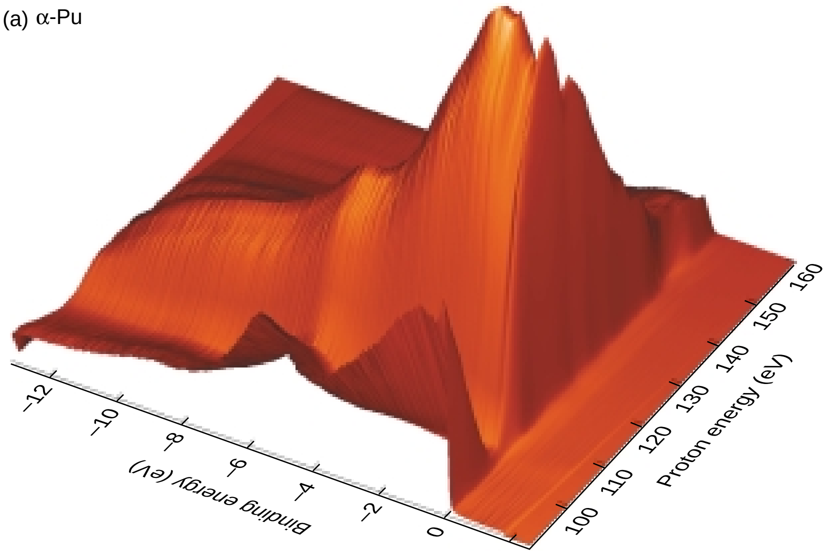


Figure 6. Cleaning of α-Plutonium by Laser Ablation

This sequence of spectra from an α-plutonium sample was taken at various stages of the laser-ablation cleaning cycle. At the start of the cycle shown in (1), the α-plutonium sample has an oxide surface, and the broad peaks are due to plutonium oxide molecular states. The features of the oxygen 2p electrons centered at E_K = 29 eV are a double peak due to oxygen band states. The large peak centered at 33.5 eV is associated with localized 5f states in plutonium oxide. As the ablation cycle proceeds, the line shape of the oxygen feature at E_K = 29 eV changes because the oxygen is no longer in a molecular state, and the density of states at the Fermi edge from the pure plutonium metal grows in intensity. By stage (5), the greatly reduced oxygen 2p signal is entirely due to adsorbed oxygen, while the localized 5f plutonium oxide state at 33.5 eV has been replaced by the metallic 5f band states. Only a few laser pulses were applied between each of the spectra shown.

(a) α-Pu



(b) δ-Pu

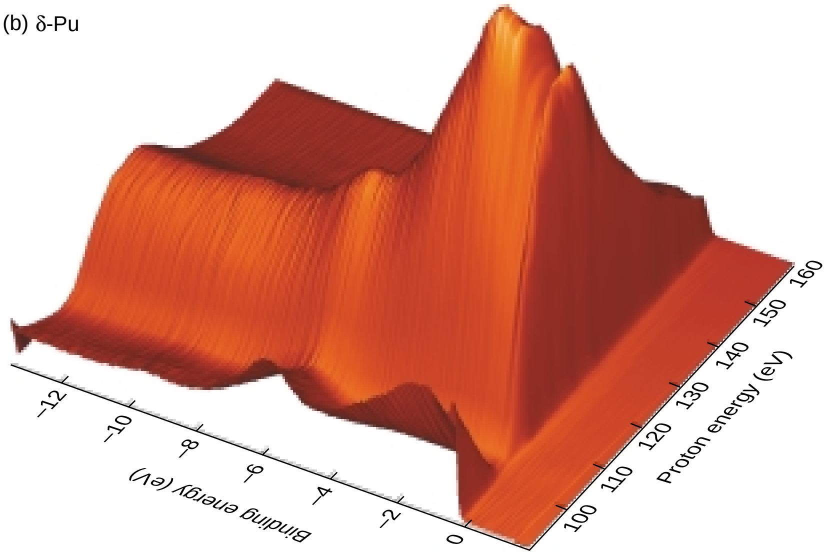


Figure 7. Valence-Band Resonant Photoemission Spectra for α- and δ-Plutonium

These three-dimensional plots of valence-band resonant photoemission spectra for (a) α-plutonium and (b) δ-plutonium were obtained at the ALS at the Lawrence Berkeley National Laboratory. The usual photoemission spectra showing intensity as a function of binding energy are plotted along a third axis, that of photon energy. The photon energy was scanned across the 5d absorption edge at about 120 eV so that one can follow intensity as a function of photon energy for a fixed binding energy (also called a CIS curve for constant initial state) through both the antiresonance and resonance energies. The spectra in both (a) and (b) show strong prominent resonance features.

unexpected results, as we show next. Lower-energy data were obtained with the LPLS system, whereas higher-energy data, including core levels, were obtained at the ALS.

PES Results for α- and δ-Plutonium

ALS Resonance Data at 300 Kelvins. Figures 7(a) and 7(b) show three-dimensional plots of resonant photoemission from α- and δ-plutonium, respectively. The α-plutonium sample was high-purity polycrystalline. The δ-plutonium sample was a small single-crystal grain (about 1 millimeter on a side) stabilized with nominally 1 weight percent (wt %) gallium and surrounded by a matrix of smaller crystallites—see Figure 5(b) in the article “Preparing Single Crystals of Gallium-Stabilized Plutonium” on page 226). Both surfaces had been cleaned to a level of oxygen on the order of 0.5 monolayer or less based on a simple calculation using peak intensities and the photoemission cross sections. The data were taken at a temperature of 300 kelvins.

The three-dimensional plots are a compilation of the standard valence-band photoemission spectra (intensity as a function of electron binding energy) for different photon energies around the primary resonance energy. Thus, at a fixed photon energy, the photoemission spectrum yields a measure of the valence-band density of states (convoluted with orbital cross sections). At a fixed electron binding energy (or fixed initial electronic state), the intensity as a function of photon energy is a measure of the photoemission cross section for that electronic state as a function of the photon energy, which is modulated by the resonant process.

From a cursory examination of the data, we can identify the salient features of the spectrum. Along the binding-energy axis, the huge intensity peak from E_F (where $E_F \equiv E_B = 0$) to about $E_B = –4$ eV constitutes the contributions from the valence bands, specifically the 7s, 5f, and 6d states of plutonium. The feature at a binding energy of about –6 eV is probably caused by the residual oxygen at the sample surface. Along the photon energy axis, the intensity minimum (about 104 eV) and maximum (approximately 120 eV) correspond to the 5d→5f antiresonance and primary resonance, respectively. These general features are similar for the α- and δ-plutonium PES measurements.

A more detailed examination reveals subtle differences in resonant behavior between α- and δ-plutonium. These differences become most evident if one examines the intensity as a function of photon energy for a fixed binding energy (usually referred to as a constant initial state, or CIS, curve). To a rough first approximation (within the one-electron approximation), CIS spectra represent the empty-state density of states convoluted with the 5d photoelectron cross section, including final-state effects. Thus, to a limited degree (governed by dipole selection rules, $\Delta\ell = \pm 1$, where ℓ is the orbital angular momentum), they give a hint of the density of states and, particularly, the 5f multiplet structure for the ($5d^9 5f^{n+1}$) configuration above the Fermi energy.

By examining the CIS spectra near the Fermi energy in Figure 7, we see that, although both the α- and the δ-allotrope show the antiresonance minimum at virtually the same point in photon energy (104 eV), the CIS curves for α-plutonium show much more structure than those for δ-plutonium. For example, the α-plutonium data have a shoulder at a photon energy of 110 eV, rising to a sharp peak at 117 eV followed by well-defined secondary features at photon energies of 123 eV, 135 eV, and 148 eV. In contrast, the δ-plutonium data show a much less pronounced shoulder at 110 eV, rising to a relatively broad, featureless peak at a 120-eV resonance energy followed by relatively less-pronounced secondary features.

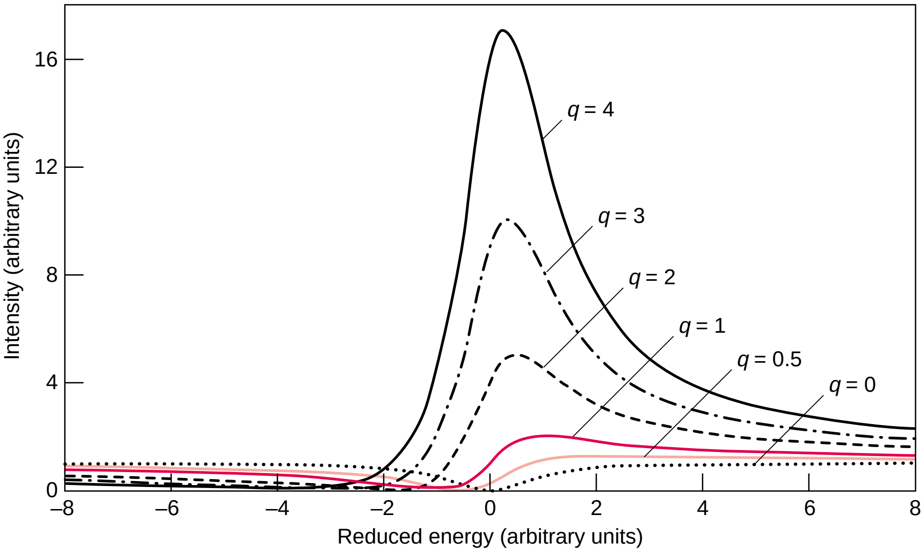


Figure 8. Calculated Fano-Line Shapes

This plot of standard Fano-line shapes as a function of the parameter *q* (basically, the intensity at resonance minus that at antiresonance) shows that the resonance peak gets sharper (the difference between the resonance and antiresonance) as the electrons involved become more localized. The shape with *q* = 1 is similar to the CIS curve for α-plutonium, and the shape with *q* = 2 is similar to the CIS curve for δ-plutonium. Thus, the resonance data suggest that the 5f electrons are more localized in δ- than in α-plutonium.

The interpretation of all the secondary features (for example, their relation to the density of states) will require supporting theoretical work, which is ongoing.

The CIS curves show a distinct Fano-line shape (see Figure 8), especially near antiresonance (104 eV). The symmetry of the curve and the magnitude of q (basically, the difference between the intensities at resonance and antiresonance) are highly dependent on the relative probabilities of resonance vs direct photoemission. The experimental CIS spectrum of δ-plutonium has a q value of 2, whereas that of α-plutonium has a q value of 1. The CIS spectrum of δ-plutonium has also a greater Fano-like symmetry. These features indicate that the relative probability for the resonant process is larger in δ- than in α-plutonium. This increase may be ascribed to an increase in electronic localization in the 5f states for the following reason. The photoabsorption cross section for the resonant 5d→5f transition (D_a) is not likely to be significantly enhanced for itinerant versus localized 5f. However, the cross section for direct 5f photoemission (D_e) is increased for itinerant electrons relative to localized electrons. The q value is given by $q = D_a/(\pi V D_e)$, where D is the matrix element for the specified transition and V is the relaxation matrix element. Thus, the Fano symmetry (and the magnitude of q) of the CIS spectrum is very sensitive to the degree of 5f electron localization. Compared with α-plutonium, δ-plutonium exhibits a greater Fano symmetry with a larger value of q, consistent with a greater degree of f electron localization.

The valence-band photoemission spectra at fixed photon energies (which are reflective of the density of states in the material to within the limitations stated in the introduction) are surprisingly similar for the two plutonium allotropes. Again, however, the data show some subtle differences. Figure 9

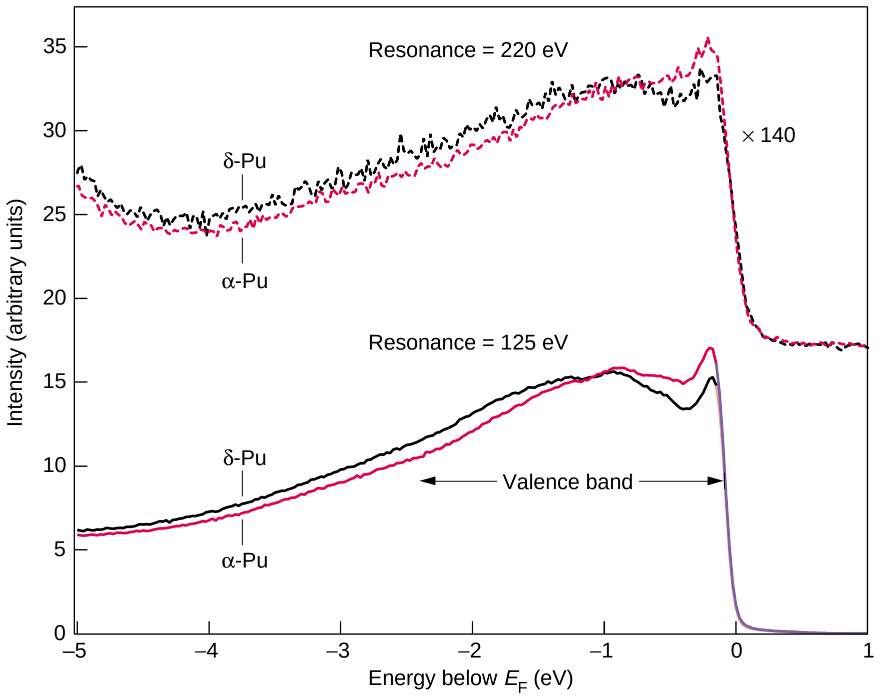


Figure 9. Spectra for α- and δ-Plutonium Near Resonance and Near the Cooper Minimum

These valence-band spectra for α- and δ-plutonium taken near resonance (hν = 125 eV) and at the Cooper minimum (hν = 220 eV) are remarkably similar. At both photon energies, the width of the emission band is about 200 meV wider in δ-plutonium than in α-plutonium, when normalized to the peak at a binding energy of ~1 eV. The increased intensity of δ-plutonium at the high binding-energy edge of the valence band may be a consequence of greater electron localization.

shows the plutonium valence-band spectra for the α- and δ-phase near resonance (hν = 125 eV) and at the Cooper minimum[3] (hν = 220 eV). At resonance (spectra at 125 eV), the δ-plutonium valence-band photoemission width extends about 200 milli-electron-volts (meV) farther below the Fermi level than the α-plutonium valence-band photoemission width.

The sharp feature near the Fermi level appears more intense in α- than in δ-plutonium. At first glance, this difference seems inconsistent with the general trend of localization in δ-plutonium. The lower intensity of the δ-plutonium feature, however, is at least partially a consequence of its narrowness—its FWHM is on the order of 70 meV. At 300 kelvins, the Fermi function is about 110 meV wide (the resolution is 10 to 90 percent of the Fermi function value), and any spectral feature of approximately this width or less located within k_BT of the Fermi energy will be affected by the Fermi function (truncated and broadened). The narrow feature in δ-plutonium falls into this category. However, temperature alone may not account for all the missing intensity relative to the data at 40 eV (see below). Some of the differences may be ascribed to different gallium concentrations in the two specimens or, perhaps, to differences in 6d admixture.

LPLS Data at 80 Kelvins. To circumvent the issue of thermal broadening and aim for a more accurate approximation of the density of states in the PES spectrum, we have collected data at 80 kelvins and 60 meV in resolution by using the sharp discharge line of a helium arc lamp at a photon energy of 41 eV. At this photon energy, the calculated 6d and 5f photoabsorption cross sections per electron are approximately equal. The surfaces were prepared by laser ablation. Figures 10(a) and 10(b) show a wide scan and an expanded view, respectively, of the resulting PES spectra for both α- and δ-plutonium. Here, the secondary electron background has been subtracted, and the integrated intensities between E_F and –4 eV are set to be equal. For this normalization, there is another slight difference in bandwidth. Globally, the two phases of plutonium appear surprisingly similar except for the narrow feature near the Fermi level, which, unlike the data at resonance in Figure 9, is now much narrower in δ- than in α-plutonium. All features observed in δ-plutonium are also found in α-plutonium, but they are much better defined in δ-plutonium, perhaps reflecting greater localization. Note that the residual feature around –6 eV represents submonolayer surface-oxygen contamination, perhaps between 0.1 and 0.2 monolayer, and is therefore ignored. For the most part, the 41-eV data are similar to those presented in Figure 9, except for the sharp features near the Fermi level in the low-temperature data.

The expanded view in Figure 10(b) shows the only clearly understandable difference between α- and δ-plutonium in the valence band data. In particular, the sharp feature in gallium-stabilized δ-plutonium is clearly much narrower than that found in α-plutonium and, to within the resolution of our spectrometer (75 meV), it crosses E_F. This feature is consistent with the larger specific-

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[3] The Cooper minimum provides a way for using a tunable light source when there is a node in the radial wave function of the initial state. By matching this node to a final-state wave function, which would give equal contributions to the positive and negative components of the transition probability, one obtains a minimum in the absorption cross section. This matching depends on the energy of the final state and thus on the incident photon energy.

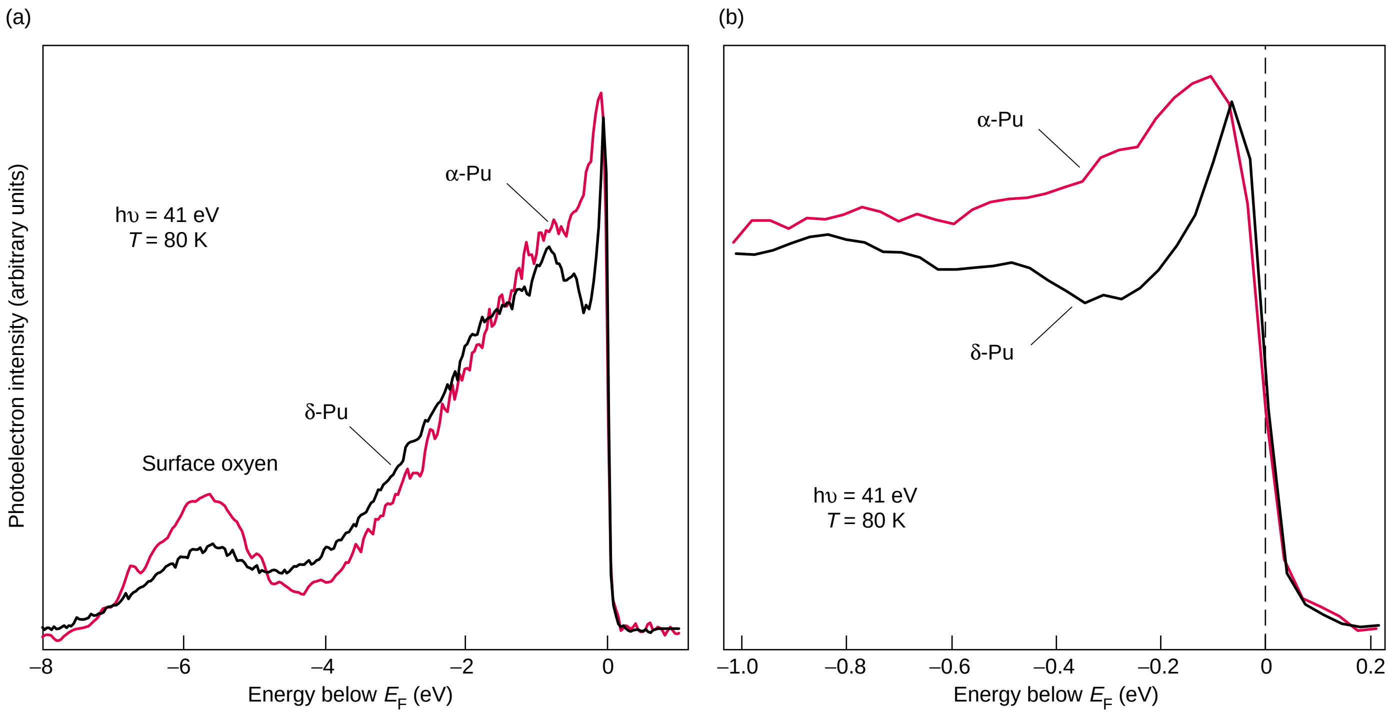


Figure 10. Spectra of α- and δ-Plutonium with Helium II Radiation

(a) In the wide-scan spectra of α- and δ-plutonium at 80 K using helium II radiation, the feature at –6 eV is due to about 0.1 monolayer of adsorbed oxygen. The secondary electron background has been removed from the spectra, and the normalization is such that the areas under the spectra, between E_F and –4eV, are equal. (b) In the expanded view of spectra near the Fermi energy, the most significant difference between the spectra is the broader near-E_F feature in α-plutonium.

heat γ-value of δ-plutonium and is similar to the feature found in spectra of uranium compounds identified as heavy fermions.

Heavy-fermion materials are metals or compounds with an unfilled 4f or 5f shell, whose specific heat and other bulk properties suggest (Lee et al. 1986) that the f electrons at the Fermi energy have a crystal effective mass larger by orders of magnitude than the rest mass of the electron and, indeed, much larger than the calculated band mass for the material. A long-standing (though simplistic) model to explain this behavior is the so-called single-impurity model (SIM) (Gunnarsson and Schonhammer 1987), which postulates that the f electrons behave as noninteracting magnetic impurities at high temperatures. As the temperature is lowered, a cloud of conduction electrons aligns antiparallel to the f spin to form a singlet state, thus quenching the magnetic moment. Within the SIM, very weak residual f-electron hybridization with this cloud produces a narrow resonance at the Fermi energy, sometimes called the Kondo resonance, which should manifest itself as a very narrow sharp feature in a photoemission spectrum. However, the applicability of the SIM to such periodic, crystalline systems is tenuous at best since the concept of an f electron “impurity” on every site (as would be required for δ-plutonium) is almost a contradiction in terms. Recent measurements in uranium heavy-fermion compounds suggest that LDA-derived bands are well reproduced experimentally, except at the Fermi energy, where the measured bands are flatter, or equivalently, narrower than the calculated bands. A comprehensive model that incorporates both lattice periodicity and electron correlations is yet to be quantified.

Temperature Dependence of the Data. One test for the applicability of the SIM to plutonium is a determination of the temperature dependence of the narrow 5f feature. In Figure 11, we show data taken at 21 eV at both 300 and 20 kelvins for α- and δ-plutonium. No change with temperature is evident in α-plutonium. On the other hand, a decrease in intensity occurs in δ-plutonium at 300 kelvins. Before interpreting this temperature dependence as evidence for the applicability of SIM, one must take into account the role of the Fermi function, which truncates this narrow feature as the temperature increases. One can approximate the effect of the 300-kelvin Fermi function by simply convoluting the data taken at 80 kelvins with a Gaussian whose FWHM is about 100 meV. This convolution broadens the narrow features at E_F but has no effect on features wider than 100 meV. With this convolution, we can fully account for the whole temperature dependence between the data at 20 and at 300 kelvins. Invoking the SIM or any other correla-

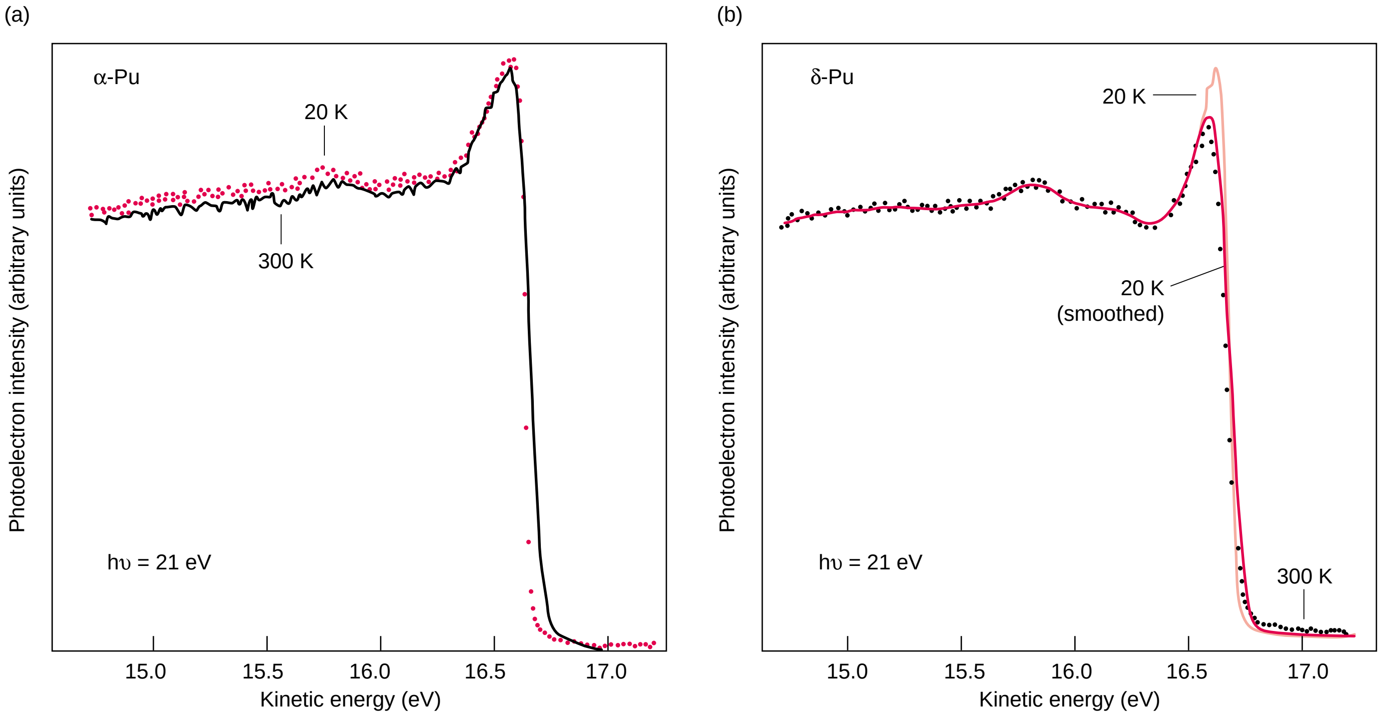
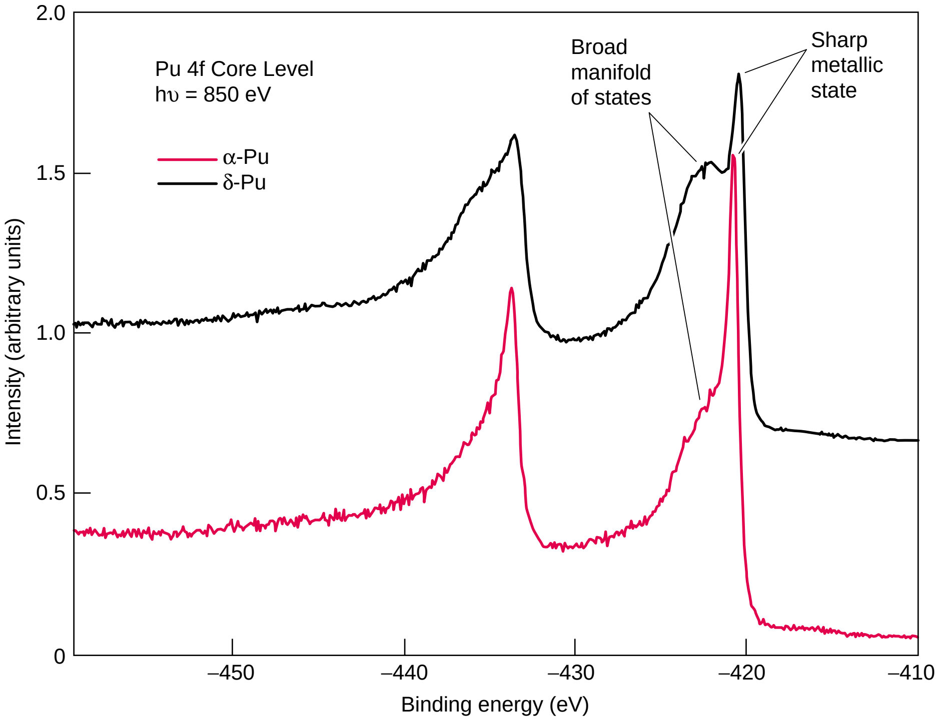


Figure 11. Spectra of α- and δ-Plutonium at 20 and 300 K

(a) Whereas α-plutonium is temperature independent, the temperature dependence of δ-plutonium (b) can be well accounted for by a convolution with an approximately 100-meV FWHM Gaussian, which approximates the Fermi function broadening at 300 K.

Figure 12. Plutonium 4f Core-Level Photoemission Spectra for α- and δ-Plutonium

The 4f core-level spectra suggest that electrons in δ-plutonium are more localized than electrons in α-plutonium. These spectra were taken at high resolution at the ALS, and the photon energy was 850 eV. In both cases, the spectra show a sharp peak at a binding energy of about −421 eV, reflecting the 4f core-level state in the metal. The core hole produced in the photoemission process is well screened from the departing photoelectron. Thus, the photoelectron reflects its initial core-level energy state. The broad peak at higher binding energies (−422 to −424 eV), by contrast, reflects a manifold of final states produced when the departing electron is poorly screened by the surrounding conduction electrons.



tion effects to explain that dependence becomes therefore unnecessary. One must use some other model (perhaps the Periodic Anderson Model or a renormalized band calculation) to explain the correlations shown as the narrow peak at the Fermi energy.

Evidence for 5f Localization in δ-Plutonium. Satellites in a 4f core-electron spectrum can shed light on the nature of the 5f states. When a core electron is ejected from an atom, the final state of the system is an atom with a core hole (a positively charged atom) and a photoelectron in the continuum. If the core hole is fully screened from the departing electron (perhaps by a refilling of the core hole on the time scale of the photoemission process), there is no electrostatic interaction between the departing electron and the core hole (no loss of energy), and the electron carries information from the initial state of the system. If, however, the screening is incomplete (as, for example, in the case of screening by a reconfiguration of the density of states around the atom), the photoelectron loses energy because of the electrostatic interaction with the positive core hole and displays characteristics that are a convolution of initial and final states.

The 4f core-level spectra in Figure 12 suggest that electrons in δ-plutonium are more localized than those in α-plutonium. These spectra were taken at the ALS at high resolution. The photon energy was 850 eV. In both cases, the spectra show a sharp peak at a binding energy of about –421 eV, reflecting the 4f core-level state in the metal. The core hole produced in the photoemission process is well screened from the departing photoelectron, and thus the photoelectron reflects its initial core-level energy state. The broad peak at higher binding energies (–422 to –424 eV), by contrast, reflects a broad manifold of final states produced when the departing electron is poorly screened by the surrounding conduction electrons. Poor screening may result when the density of states of the electrons at the Fermi energy is low or when the electron mobility is poor because these electrons have a large effective mass (that is, they exibit correlation behavior).
By comparing the α- and δ-plutonium spectra, we find that δ-plutonium shows a greater percentage of poorly screened final-state events than α-plutonium. This result suggests that δ-plutonium has fewer mobile (delocalized) electrons available for screening of the core hole, which is consistent with δ-plutonium having a narrow f band and its f electrons having a larger effective mass and hence being more localized. The core-level results are consistent with the valence-band PES data.

Ruling out Surface Effects. In the past, questions were raised about the possibility that α-plutonium may contain a δ-like surface structure. Indeed, the similarities of the PES spectra would seem to suggest such a possibility. However, the more-bulk-sensitive spectra at 220 eV appear similar to those at resonance (125 eV) and at 40 eV and would indicate that, in all cases, we are observing bulk features and that the small differences

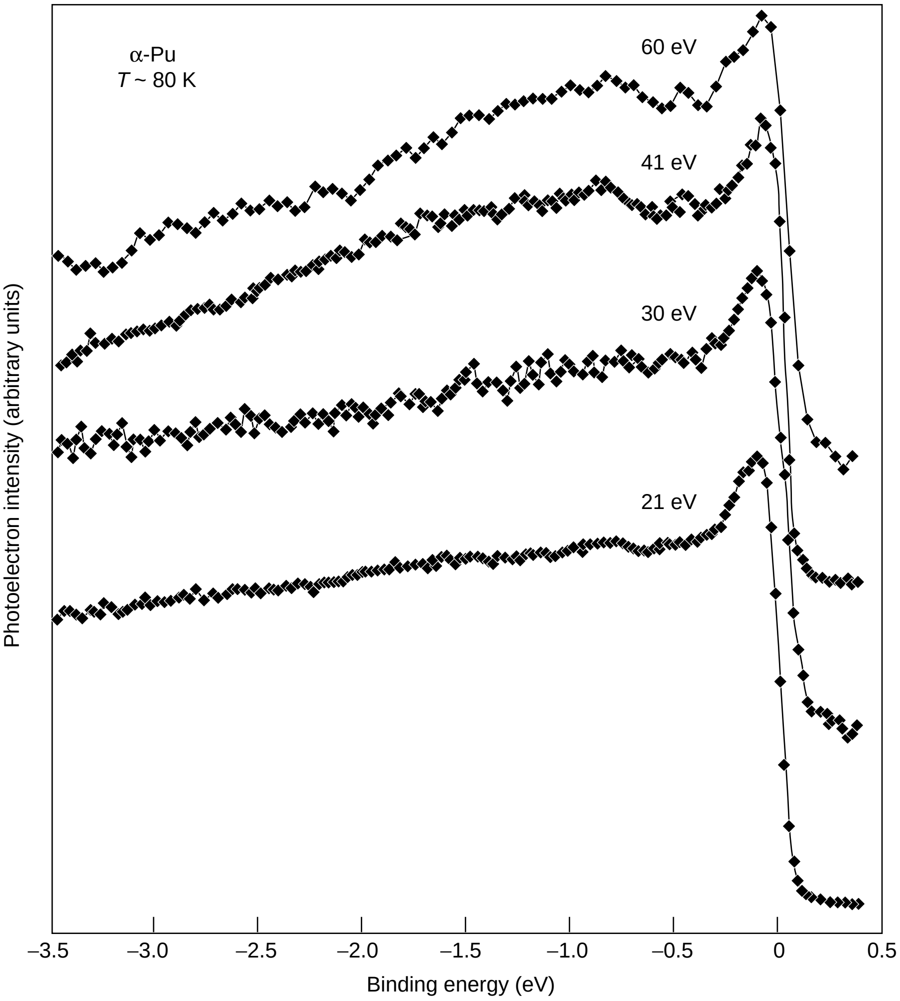


Figure 13. Spectra of α-Plutonium at 80 K and Several Photon Energies
The narrow feature near E_F is persistent at all photon energies and must thus contain substantial 6d admixture in its orbital symmetry. At 21 eV, the photoemission should be dominated by 6d emission (see Figure 4). Moreover, it is most likely bulk-derived based on the larger escape depth at 21 eV. The purer 5f states are in the region of –1 eV. That region clearly grows faster with photon energy than the near-E_F peak.

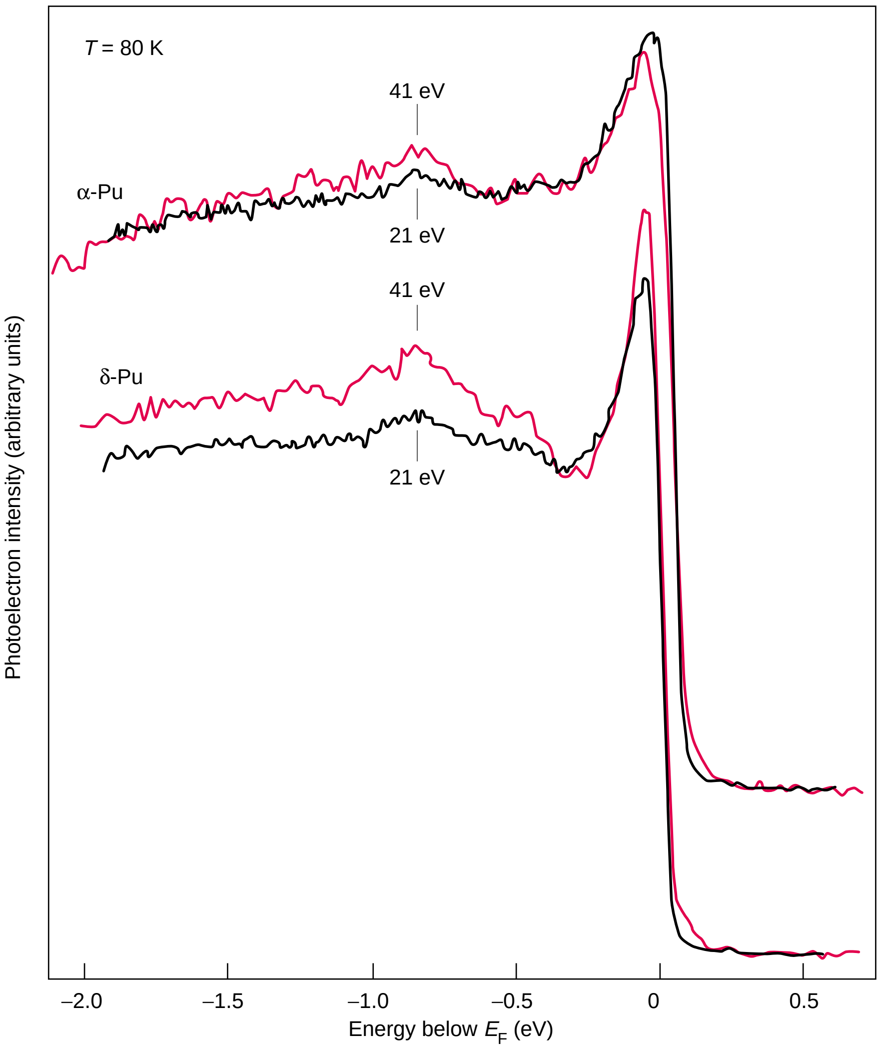


Figure 14. Spectra of α- and δ-Plutonium at 21 and 41 eV and at 80 K
Data at 21 eV (black lines) and 41 eV (red lines) and a temperature of 80 K for α- and δ-plutonium are overlaid to show relative peak intensities of the near-E_F features. There is a noticeable increase in the 5f vs 6d character in δ-plutonium.

between α- and δ-plutonium are bulk derived. Further, this assumption suggests that α-plutonium does not exhibit a δ-like surface. This conclusion is additionally corroborated by spectra at lower photon energies. At these energies, PES measurements using 21-eV photons yield even greater bulk sensitivity than those using 220-eV photons (see Figure 2). In Figure 13, we show α-plutonium PES spectra taken at 80 kelvins with 21-, 30-, 41-, and 60-eV photons. The sharp feature at E_F is, in fact, somewhat more intense relative to the other features in the 21-eV spectrum than in the spectra at higher energies, which indicates not only that this peak derives from the bulk, but also that it contains more 6d admixture in its orbital character than the remaining features, which may be more 5f in character.

A similar plot for δ-plutonium (see Figure 14) reveals that we are again dealing with bulk phenomena because the 21-eV data are similar to the 41-eV data. In this case, however, the intensity of the sharp peak at E_F relative to other features increases significantly from the 21-eV spectrum to the 41-eV spectrum. This result indicates that the near-E_F peak contains more 5f character in δ- than in α-plutonium. The near invariance of the relative intensities of the features with photon energy points to a relatively uniform admixture of 6d character throughout the valence band region (compare these data to the NpAs data illustrated in Figure 4). Irrespective of the amount of 6d admixture, the spectrum is consistent with the very narrow band behavior observed in bulk properties and with the conventional wisdom that the 5f states in α-plutonium are more hybridized and band-like than those in δ-plutonium.

Surface reconstruction is common for metals throughout the periodic table. In general, however, it is only observable in high-quality single crystals, and even then, one must distinguish between a reconstructed surface and simply a surface termination layer. Although interpretations of previous data suggested that the crystal structure on the surface of α-material would become δ-like, the dependence of normal emission spectra on photoelectron escape depth measured by varying the photon energy was not available. Our new measurements of the α-plutonium spectra as a function of escape depth yield nearly invariant spectra, strongly suggesting a lack of reconstruction (from α- to δ-material).

Current understanding would indicate that we have indeed measured the bulk electronic structure of α- and δ-plutonium. All data are consistent with the concept of much narrower itinerant states in the δ- than in the α-phase of plutonium. Indeed, bulk property data for δ-plutonium suggest behavior like that of heavy fermions. However, very narrow bands are already obtained within a constrained band calculation (see the article “Actinide Ground-State Properties” on page 128). An additional electric-field component acts on the 5f electrons within this generalized-gradient approximation (GGA), which is a refinement of the traditional local-density approximation (LDA), the workhorse of density functional theory. These bandwidths in the constrained calculation agree, to some extent, with the experimental bandwidths in δ-plutonium. Thus, there may be no need for further band narrowing such as might result from additional correlation effects (see the comparison with calculations in the article "Electronic Structure of α- and δ-Plutonium" on page 152). Note that, by constraining some of the 5f electrons to be localized in the above-mentioned GGA calculation, one has already introduced substantial correlation effects.

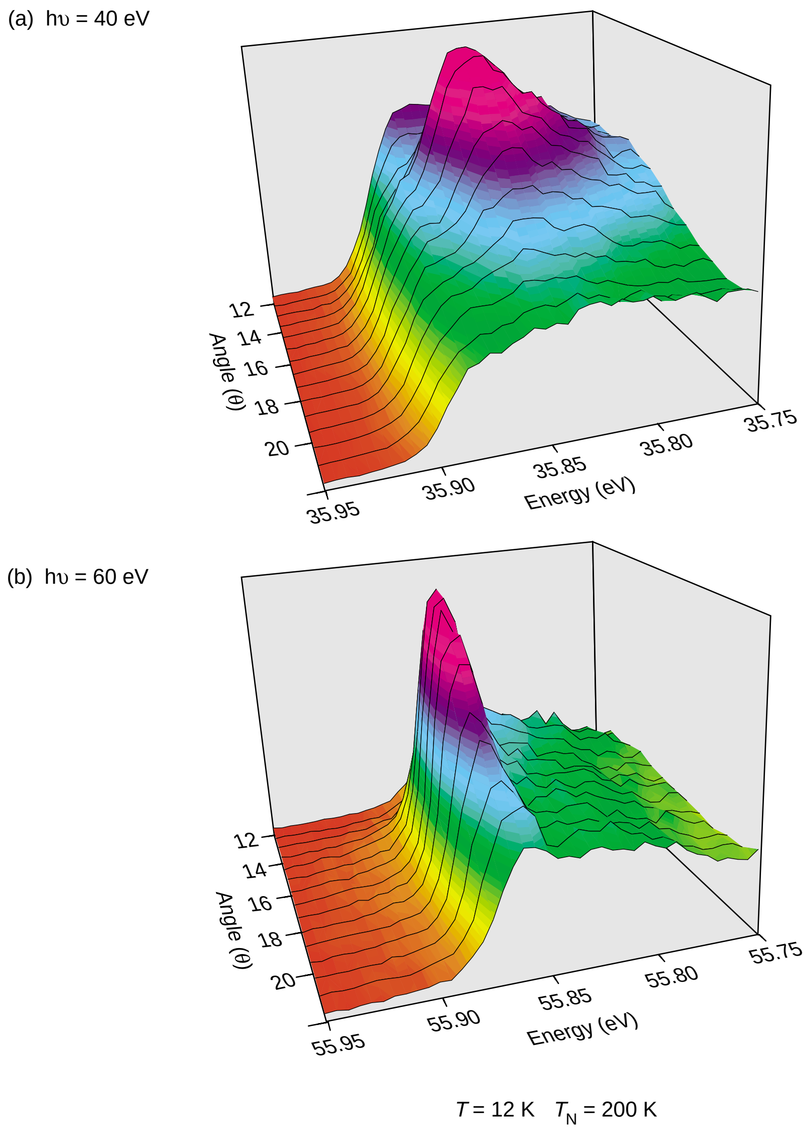


Figure 15. Angle-Resolved PES Data for Antiferromagnetic USb_2

This is essentially *E* vs *k* dispersion, with *k* represented by the angle (1 degree = 0.07 Å^{-1} for 60-eV data and 0.06 Å^{-1} for 40-eV data). Only the first 200 meV within the Fermi energy are shown. The 40-eV data in (a) are primarily sensitive to 6d emission, whereas the 60-eV data in (b) represent primarily 5f emission. Note that both 6d and 5f bands show dispersion and that the 5f intensity disperses below the Fermi energy. The center of the Brillouin zone is near 18°.

The Need for Single Crystals. Many of the remaining questions on plutonium and its compounds or alloys will be resolved once data are obtained on high-quality single-crystal materials. For photoemission experiments, these crystals should have mirror surfaces and well-defined axes normal to the surface. A glimpse of this future can be observed in Figure 15, in which we show angle-resolved spectra on a high-quality single crystal of the uranium-antimony compound USb_2 grown[4] by precipitation from a flux. In addition to reflecting the high quality of the crystal, the data in Figure 15 represent state-of-the-art resolution (15 meV) obtained with a state-of-the-art detector (the Scienta), which simultaneously preserves energy and angle information. Each scan of the Scienta simultaneously measures up to 100 electron emission angles (relative to the sample surface) and, hence, 100 spectra. Using this apparatus at a high-intensity undulator beamline (at the Synchrotron Radiation Center in Madison, Wisconsin) produces the dramatic spectra of Figure 15. The figure shows only the first 200 meV of the valence bands below the Fermi energy. The data at 40-eV photon energy in (a) contain contributions mainly from d states, whereas the data at 60-eV photon energy in (b) derive primarily from the 5f electrons. The three-dimensional plot in (b) clearly shows that the 5f intensity in antiferromagnetic USb_2 is confined to a narrow portion of the Brillouin zone. As the 5f band hybridizes with the 6d electrons, it disperses away from the Fermi energy, and the quasiparticle peaks broaden and diminish to near zero. The center of the Brillouin zone is located near the 18° angle. One can see that there is no 5f intensity whatsoever at angles larger than about 23°. This constitutes a classic case of f-d

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[4] John Sarrao of Los Alamos grew this single crystal.

hybridization. Similar-quality single crystals of plutonium compounds have recently been grown with flux growth techniques.[5] Data such as those in Figure 15 could therefore be obtained for plutonium compounds with a Scienta energy and angle analyzer. It should then be possible to view the band structure of these plutonium compounds directly.

Conclusions

The large photon fluxes now available from bright, low-emittance undulator beamlines have made it possible to perform some photoemission experiments on plutonium at synchrotron sources. This development will enhance our knowledge of the electronic structure of this material. We have also developed the LPLS as a viable source for conducting photoemission experiments within a conventional laboratory environment. With intensities rivaling those of second-generation synchrotrons, the LPLS is particularly useful for those experiments on hazardous materials that benefit from a highly controlled and contained environment. A combination of PES tools will be used to tackle the least studied, yet the most interesting, series in condensed matter physics—the transuranics.

Results on α- and δ-plutonium suggest that the electronic structure is characterized by an intense, sharp feature of mixed 5f and 6d character near the Fermi energy, as well as a manifold of broad 5f features centered at a binding energy of about –1 eV. The sharp feature near the Fermi energy is much broader in α- than in δ-plutonium, consistent with stronger hybridization. The intense, narrow 5f peak in δ-plutonium is reminiscent of the sharp features in cerium compounds referred to as a Kondo resonance, but this feature appears to be reproduced in a GGA band calculation that constrains some of the 5f electrons to be localized. The use of periodic models based on the Anderson Hamiltonian may be eventually necessary for modeling the electronic structure of δ-plutonium, but the constrained GGA result for δ-plutonium provides a reasonable starting point. The similarity between α- and δ-plutonium spectra raises suspicion about a surface reconstruction in α-plutonium to a δ-like surface, particularly since the sharp feature in α-plutonium is not reproduced in a band calculation. However, measurements with varying escape depths do not support this notion. Future measurements on single crystals will open a whole new field of study for plutonium materials. ■

Further Reading

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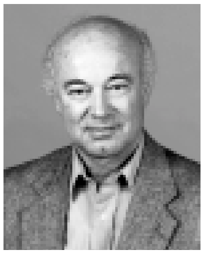
[5] In April 2000, John Sarrao of Los Alamos has grown single crystals of the compounds $PuIn_3$, $PuGa_3$, and $PuSn_3$.



Aloysius J. Arko received his Ph.D. in condensed matter physics from Northwestern University. He is currently a staff member at the Los Alamos National Laboratory. His primary research interest has been photoelectron spectroscopy in narrow-band materials. Arko is a Fellow of the American Physical Society and of Los Alamos National Laboratory. In recognition of his contributions to the Laboratory, Arko received the Los Alamos Fellows Prize and the Distinguished Performance Award. His recent interests are increasingly directed toward the study of plutonium and its compounds with the unique photoemission capabilities of the laser-plasma light source.

John J. Joyce received a B.A. in Physics *Summa Cum Laude* from St. Mary's University and a Ph.D. in Materials Science from the University of Wisconsin. He has conducted photoemission research, the results of which have been published in over 80 articles and presented in 50 invited and contributed talks. John joined the Laboratory in 1990. His current research interests include electronic properties of rare earths and actinides with photoemission research conducted at the Synchrotron Radiation Center and the Laser Plasma Light Source (LPLS). He is a member of the Advisory Committee for the Synchrotron Radiation Center and one of the principal investigators on the LPLS project. For his work on the LPLS, John received the Los Alamos Distinguished Performance Award and the Los Alamos Achievement Award.

Luis A. Morales received his undergraduate degree in chemistry from Arkansas State University and his Ph.D. from the University of Kansas, where he was in the High-Temperature/ Materials Science group. After a postdoctoral stint at Los Alamos National Laboratory, Luis became a staff member in the Nuclear Materials and Technology group. His research interests cover areas of solid state and solid-gas phase chemistry. In order to understand structure-property relationships, Luis applies aspects of thermodynamics, kinetics, and crystallography to actinide-containing chemical systems.

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Roland K. Schulze received his B.S. in chemistry from the University of Minnesota, Duluth, and his Ph.D. in chemistry from the University of Minnesota, Minneapolis. Roland joined the Los Alamos Laboratory as a postdoctoral fellow in the Analytical Chemistry Group, where he conducted surface science research and developed and built a time-of-flight secondary ion mass spectrometer for surface and interface studies. Since becoming a technical staff member, Roland has been with the Materials Characterization Team in the Chemical and Metallurgical Research (CMR) Facility, first in the Materials Science and currently in the Nuclear Materials Division. In the past four years, he has built up an analytical surface-science facility in the CMR to study radiological materials and perform fundamental measurements on actinide solids. Roland's research interests include the surface chemical behavior of actinide solids, mineral surface interactions with molecular actinides in environmental situations, and the electronic structure of actinide materials.