

The Actinide Research Quarterly

Los Alamos National Laboratory
Nuclear Materials Research and Technology
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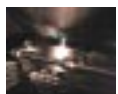
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$^{239}\text{Pu}/^{240}\text{Pu}$ Isotope Ratios Can Be Determined Using LIBS

Laser Induced Breakdown Spectroscopy (LIBS) is also known as laser ablation/optical emission spectroscopy. This type of high-resolution emission spectroscopy has received considerable attention as a versatile analytical technique. The technique has several advantages over other forms of analysis for nuclear applications; those of greatest importance at the Los Alamos Plutonium Facility include reduction of sample size, direct analysis in inhomogeneous matrices, reduced turnaround time between sample submittal and results, and *in-situ* analysis capability. The Plutonium Facility currently employs standard inductively coupled plasma mass spectrometry/atomic emission spectroscopy for most chemical analyses, with dissolution of a fairly large sample (~ 0.5 g) normally required. Isotope ratios are determined by thermal ionization mass spectrometry (TIMS) or gamma spectrometry. LIBS has been previously applied to actinide analysis, including recent work involving U isotope ratio determination.

Observation of isotope shifts through the use of optical emission spectroscopy is not a common application for LIBS, mainly because of the very high resolution needed. However, a French research group at CEA Saclay has recently reported a LIBS isotope ratio determination for uranium using the U(II) line at 424.437 nm with a $^{238}\text{U}/^{235}\text{U}$ isotope shift of 1.39 cm^{-1} (0.025 nm). Their observed linewidth of 0.67 cm^{-1} (0.012 nm) was approximately twice as broad as the instrument limit

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Figure 1. A LIBS plasma plume produced from a lump of electrorefined Pu metal. The laser impinges on the sample vertically from the top, with emission collected horizontally by the 40 mm diameter, f/3 lens at far left. The sample chamber viewport is approx. 2.5" in diameter.

$^{239}\text{Pu}/^{240}\text{Pu}$ Isotope Ratios Can Be Determined Using LIBS (*continued*)

This article was contributed by Coleman A. Smith (NMT-11). Other researchers on the project include Max A. Martinez and D. Kirk Veirs (NMT-11 and David A. Cremers (C-1).

of 0.305 cm^{-1} (0.0055 nm). This linewidth was produced using experimental conditions of 308-nm laser wavelength, 0.46-GW/cm^2 focused laser energy density, a delay time of $<500\text{ ns}$, and 3 Pa ($\sim 20\text{ mtorr}$) of air as the buffer gas.

One of the largest plutonium isotope shifts occurs in the Pu(I) emission line at 594.52202 nm , which has a $^{239}\text{Pu}/^{240}\text{Pu}$ isotope shift of 0.355 cm^{-1} , approximately one-fourth of the isotope shift of the U(II) transition. The smaller value for this isotope shift is partially due to the 1 atomic mass unit (amu) difference between common Pu isotopes as compared to the 3-amu difference between the two most abundant natural isotopes of uranium. This small isotope shift makes an isotope ratio determination more challenging. Under the experimental conditions reported for the observation of the uranium isotope ratio, where the linewidth is 0.67 cm^{-1} , the emission from the plutonium isotopes would not be resolved, and an isotopic ratio measurement of $^{239}\text{Pu}/^{240}\text{Pu}$ using LIBS would not be possible. The linewidth reported in the French work is attributed to Doppler and Stark broadening in the very hot plasma of the French experiment. A higher buffer-gas pressure and longer delay times should result in a cooler plasma, in which smaller isotope shifts may be observed. We show that this approach allows the LIBS measurement of the $^{239}\text{Pu}/^{240}\text{Pu}$ isotope ratio.

The LIBS system employs the following major components: a pulsed laser, sample chamber, emission spectrometer, detector, and computer. Work within the Plutonium Facility requires that radioactive samples be contained inside a glove box. Only the sample chamber and a minimum of optics reside within the glove box (see Figure 1); all other optical components are mounted on external optical tables. A pulsed and Q-switched Nd:YAG laser was used, operating at its fundamental wavelength of 1064 nm and generating pulse widths of $\sim 5\text{ ns}$. The laser energy is typically attenuated to $\sim 25\text{ mJ}$ and focused into a $<100\text{-mm}$ spot on the sample surface, producing an

energy density of $\sim 10^{11}\text{ W/cm}^2$. This high energy density is sufficient to both vaporize the sample surface and to generate a high-temperature plasma consisting of both neutral atoms and ions. The plasma species are electronically excited and emit light characteristic of all elements present in the ablation plume. The sample is enclosed in a vacuum chamber that is backfilled with helium at 100 torr pressure. This atmosphere allows some translational and electronic cooling of the plasma without excessive quenching of the emission. The emission is collected and collimated before exiting the glove box through a second viewport. The light is then focused onto the entrance slit of a high-resolution spectrometer, where it is wavelength-dispersed and collected on an intensified charge-coupled device (ICCD) camera. A broad continuum emission background is avoided by electronically delaying the ICCD by 1 ms following the laser pulse collecting the emission over a gate width of 5 ms.

A Pu transition was selected for analysis based on its large isotope shift, high intensity, and minimal spectral interference from neighboring lines. Atomic emission dominates the plasma at longer ICCD delay times, and as the plasma cools, expansion slows, thus allowing more electron-ion recombinations to occur. As a result, atomic emission is favored because of a decrease in both Doppler and Stark line broadening. Thus, the Pu atomic line at 594.52202 nm (16815.576 cm^{-1}) was chosen for this work, with a previously observed $^{239}\text{Pu}/^{240}\text{Pu}$ isotope shift of 0.355 cm^{-1} .

Two samples of greatly differing isotopic composition were chosen for characterization. The first sample consisted of Pu metal of a nominal 239/240 isotopic ratio of 93/6. The second sample was PuO_2 with a nominal ratio of 49/51. The oxide sample was analyzed as a pressed pellet.

The $^{239}\text{Pu}/^{240}\text{Pu}$ isotope shift of 0.355 cm^{-1} from the plutonium atomic line at 594.52202 nm is clearly resolved in our plasma conditions (see Figure 2). Curve-fitting yields integrated peak-area ratios that match isotopic ratios as measured by TIMS or gamma spectrometry within $\pm 0.5\%$. The curve fit typically produces a peak separation of ~ 6.7 pixels, with full-width-at-half-maximum at ~ 3.2 pixels. The observed plutonium linewidths are calculated to be 0.19 cm^{-1} (0.0067 nm) based on the known dispersion of the spectrometer. These linewidths are within the experimental error of the ideal instrument-limited linewidth, which is calculated to be 0.15 cm^{-1} (0.0052 nm) based upon the known modulation transfer function for the ICCD system.

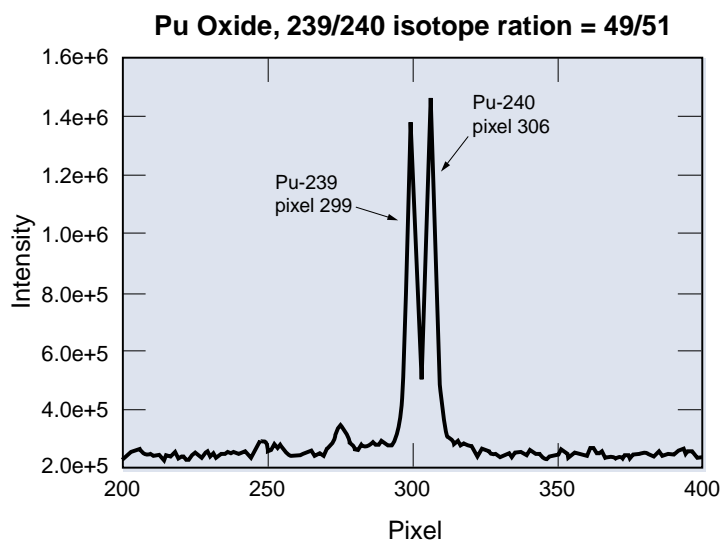
In the uranium work by the French group, the uranium plasma is dominated by ionic lines that exhibit a larger degree of broadening. They study the $^{238}\text{U}/^{235}\text{U}$ isotope shift using an ionic line at 424.437 nm with an isotope shift of 0.025 nm , or 1.39 cm^{-1} , and report line broadening exceeding the instrument limit by a factor of 2 (observed linewidth $\sim 0.012\text{ nm}$, instrument limit 0.0055 nm). A Doppler width of 0.0106 nm was calculated for the U(II) line, with Stark width $\sim 0.002\text{ nm}$ at a delay time of 350 ns and $\sim 20\text{ mtorr}$ buffer-gas pressure.

Although the experimental apparatus used by the French group closely resembles that of our work, there are major differences in the experimental conditions that greatly affect intrinsic linewidth. In particular, our conditions of increased buffer gas pressure and longer delay time allow the plasma to achieve much lower translational temperatures, in spite of much higher laser energy densities. The use of a longer wavelength emission line for analysis provides greater peak separation. These effects result in smaller linewidths and adequate resolution that allow the plutonium isotopic ratio to be determined. The linewidths observed under our conditions for plutonium

should be applicable to all of the light actinides (Th-Cm) under the same experimental conditions because the first ionization potentials are similar, ranging from 5.97 eV for Am to 6.27 eV for Np, and changes in the relative masses are small. Since the reported largest isotope shifts for Pu and U are in the range of $0.3\text{--}0.5\text{ cm}^{-1}/\text{amu}$, the isotopic shifts for all of the light actinides should be similar, and LIBS should be applicable for isotopic ratio determinations across the light actinide series.

We have shown that LIBS may be applied to plutonium isotopic analysis. The technique is sensitive, essentially nondestructive, and can produce accurate results with reasonable precision. The accuracy of the technique critically depends on adequate spectral resolution of isotopic emission. We find that our conditions are well suited to resolution of 1-amu isotope shifts, and we expect that analysis of all actinides are possible under our conditions, of which the most important are long delay times and high buffer-gas pressures.

Figure 2. LIBS produced a one-dimensional spectrum of the Pu emission line from $^{239}\text{Pu}/^{240}\text{Pu}$ isotopes in PuO_2 at 594.52202 nm , clearly showing resolution of the $^{239}\text{Pu}/^{240}\text{Pu}$ isotope shift. The LIBS setup at Los Alamos produces conditions better suited to such fine discriminations in actinides than a similar French experiment does (recently conducted at CEA Saclay).



Studies of Actinide Perfluorodiphenylamido Complexes Support Science Mission

This article was contributed by **Susan M. Oldham** and **Ann R Schake** (NMT-5); **Arthur N. Morgan III** (NMT-11); and **Brian L. Scott, Benjamin P. Warner,** and **John G. Watkin** (C-SIC).

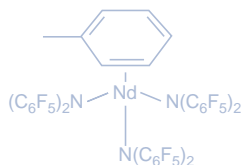


Figure 1. Trisamido neodymium complex.

Fundamental chemistry of the actinide elements provides important support for the mission at Los Alamos. In contrast to other aspects of plutonium research, details of its molecular chemistry remain relatively unknown. This knowledge, however, can provide the basis for understanding important metallurgical properties relevant to the weapons mission and development of process-related chemistry and separation chemistry, as well as benefiting the Shelf Life Extension, Enhanced Surveillance, and Stockpile Stewardship Programs.

Our goal is to elucidate the fundamental chemistry of the actinides by focusing our efforts on preparation and characterization of simple, well-defined systems and comparing their molecular structure and reactivity to well studied lanthanide and transition metal analogs. The subject of this article is our work in preparing a set of actinide complexes supported by amido ligands. The first uranium amido complex was reported in 1956 by Gilman and coworkers at Iowa State College, detailing their efforts to prepare volatile uranium complexes for the Manhattan Project. Tetrakis(diethylamido) uranium was prepared by the reaction of the lithium salt of the amine with uranium tetrachloride and then isolated by distillation under reduced pressure. Other actinide amido complexes have also been reported to be volatile. The tris(silylamido) complexes of uranium, neptunium, and plutonium sublime around 60°C at 10⁻⁴–10⁻⁵ Torr.

Currently, several research groups in North America, Great Britain, and Europe are actively investigating actinide amido complexes, principally as well-defined precursor materials for synthetic chemistry. Recent interest lies in

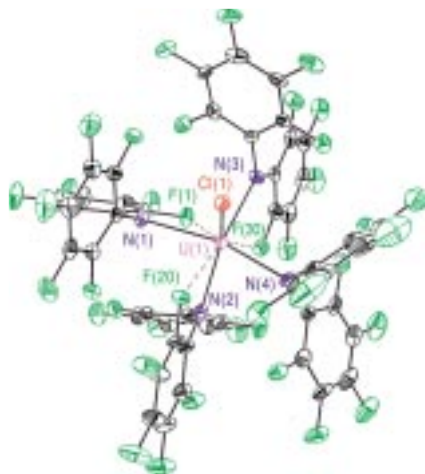


Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) for [Na(thf)₅][U(N(C₆F₅)₂)₄Cl]. For clarity, the [Na(thf)₅]⁺ counter ion has been omitted. Characterization of actinide amido complexes helps to elucidate the fundamental chemistry of the actinide elements.

their rich reaction chemistry, including activation of molecular nitrogen. Homoleptic tetra- and tri-amido complexes are generally soluble in common organic solvents and are therefore valuable entries in the synthesis of moisture-sensitive organometallic complexes of the +4 and +3 oxidation states. With the dual goals of exploring the electrophilic chemistry of the actinide elements and also developing volatile organometallic actinide complexes for chemical vapor deposition applications, we have set out to prepare a series of Th, U, Np, and Pu complexes stabilized by perfluorodiphenylamido ligands—N(C₆F₅)₂.

Perfluorodiphenylamido ligands have been used previously to stabilize highly electrophilic lanthanide complexes. X-ray diffraction studies have revealed that the lanthanide amido unit is quite electrophilic and readily forms weak intramolecular interactions to saturate the coordination sphere of the large lanthanide(III) ions. Of note is the (trisamido) neodymium complex (h⁶-C₆H₅Me)Nd[N(C₆F₅)₂]₃ (Fig. 1) that coordinates an h⁶-bound toluene solvent molecule as well as three significant Nd-F interactions (2.6 to 2.7 Å) and one weak Nd-F interaction (2.9 Å).

Recently we have synthesized several novel uranium amido complexes that have been characterized by single-crystal x-ray diffraction. The electrophilic nature of these complexes is exemplified by the reaction of UCl₄ with four equivalents of NaN(C₆F₅)₂ in tetrahydrofuran (THF). Crystallization from toluene yields lime crystals of the “ate” complex [Na(thf)₅][U(N(C₆F₅)₂)₄Cl], in which one chloride ligand remains coordinated to the uranium metal center to yield an anionic U(IV) complex (Fig. 2). Close intramolecular contacts between three *ortho*-fluorine atoms and uranium (2.6 to 2.7 Å) further testify to the electron deficiency of the uranium atom.

This result was unexpected since we hoped to synthesize the homoleptic U(IV) amido complex; however, there is precedence of the formation of “ate” complexes. In France in 1998 Ephritikhine prepared the [Li][U(NEt₂)₄Cl] analogue during his attempts to synthesize U(NEt₂)₄. The average U-N bond lengths of the two complexes are similar with [Li][U(NEt₂)₄Cl] measuring 2.37 Å and [Na(thf)₅][U(N(C₆F₅)₂)₄Cl] measuring 2.386 Å.

While Ephritikhine reports that several extractions of $[\text{Li}][\text{U}(\text{NEt}_2)_4\text{Cl}]$ with ether allows for the complete removal of LiCl and the formation of $\text{U}(\text{NEt}_2)_4$, we find that reaction of UCl_4 with four equivalents of $\text{NaN}(\text{C}_6\text{F}_5)_2$ in THF conducted under more concentrated conditions does yield the desired homoleptic tetrakisamido complex $\text{U}[\text{N}(\text{C}_6\text{F}_5)_2]_4$. Interestingly, actinide complexes supported by less bulky amido ligands readily form dimeric (Fig. 3), or trimeric (Fig. 4) structures. The homoleptic diethylamido and dimethylamido uranium(IV) complexes are shown below.

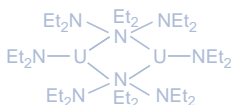


Figure 3. Dimeric actinide amido complex

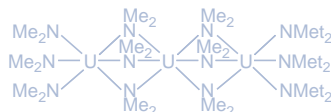


Figure 4. Trimeric actinide amido complex.

The single-crystal x-ray structure of our red tetrakisamido complex (Fig. 5) is very similar to that of the nonfluorinated diphenylamido complex. Each monomeric uranium metal center is coordinated to four nitrogen atoms in a distorted tetrahedral structure. The uranium nitrogen bond lengths of the fluorinated and non-fluorinated complexes are almost identical with averages of 2.26 and 2.27 Å, respectively. The tetrakis(perfluorodiphenylamido) uranium complex also has contacts between the uranium metal center and three fluorine atoms, although they are slightly weaker than those in the "ate" complex (2.8-2.9 Å). This complex is the subject of ongoing reactivity and volatility studies.

Reaction of $[\text{UO}_2\text{Cl}_2(\text{thf})_2]_2$ with four equivalents of $\text{NaN}(\text{C}_6\text{F}_5)_2$ in THF yields the red uranyldiamido complex $\text{UO}_2(\text{N}(\text{C}_6\text{F}_5)_2)_2(\text{thf})_2$. The single-crystal x-ray structure reveals an octahedral coordination environment around the uranium metal center. The linear uranyl unit is augmented by two trans amido ligands as well as two tetrahydrofuran solvent molecules (Fig. 6).

Examples of structurally characterized uranyl amido complexes are rare. A comparison can be made between our uranyl amido complex and uranyl alkoxide complexes. The uranyl moiety in the bis(perfluorodiphenylamido) uranyl complex is shortened, with an average U-O bond length of 1.75 Å compared to those of uranyl alkoxide complexes with typical bond lengths between 1.77-1.79 Å.

We are also attempting to prepare triamido complexes of plutonium(III) and neptunium(III). The tris(silylamido) complexes of neptunium and plutonium are the only amido complexes reported for transuranic metals. Starting from the tris(silylamido) complexes we have employed an aminolysis reaction. Reaction of three equivalents of perfluorodiphenylamine with the blue-black tris(silylamido) neptunium(III) complex in hexane forms an insoluble yellow product that is subsequently filtered from the solution and dried in vacuo. Fluorine nuclear magnetic resonance (NMR) spectroscopy of the neptunium complex shows resonances that have shifted from those of free ligand; however, the data are inconclusive, and therefore complete characterization is difficult. Similar reaction of three equivalents of perfluorodiphenylamine with the orange tris(silylamido) plutonium(III) complex in hexane forms an insoluble light-purple product that is also filtered off and dried in vacuo. Attempts to grow single crystals of these transuranic complexes have been unsuccessful to date. Further NMR studies and crystallization attempts of both the neptunium and plutonium complexes will resume in PF-4 during the second quarter of FY01.

Our work has extended the library of actinide complexes. Novel uranium amido complexes have been synthesized and characterized by single-crystal x-ray diffraction. The reaction chemistry of perfluorodiphenylamine with both neptunium and plutonium shows interesting initial results. We are hopeful that complete characterization of these transuranic complexes will be possible.

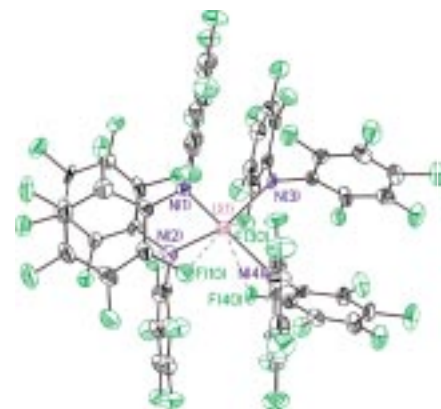


Figure 5. Thermal ellipsoid plot (30% probability ellipsoids) for $\text{U}[\text{N}(\text{C}_6\text{F}_5)_2]_4$.

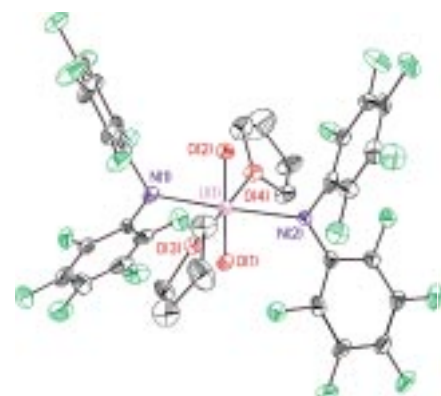


Figure 6. Thermal ellipsoid plot (30% probability ellipsoids) for $\text{UO}_2(\text{N}(\text{C}_6\text{F}_5)_2)_2(\text{thf})_2$.

Editorial

Actinide Research Quarterly Celebrates a Six-Year Anniversary—A Challenging Time

This editorial was contributed by **Kyu C. Kim**, NMT Chief Scientist.

This issue of the *Actinide Research Quarterly* marks the sixth year anniversary of this publication, a significant accomplishment in technical news reporting by a part-time, three-person publication team. We have not missed a single quarter except the summer of this year when we combined the 2nd and 3rd quarters for the timely reporting of the “Plutonium Futures - The Science” conference with extended coverage of this international conference, held in Santa Fe in July.

Six years ago we started out with the simple objective of highlighting recent achievements and ongoing programs of the Nuclear Materials Technology (NMT) Division. In the beginning we did not have a very good idea about who might read the newsletter and what might constitute readable materials in a technical newsletter.

What has worried me additionally is, “Can we continue to tap enough source materials to report and write about quarter after quarter?”

While the NMT organization is large, its programmatic activities complex and diverse, and its mission and national goals compelling, it is not a daily event, or even a monthly event to record technical successes and accomplishments year after year.

Every quarter brings unique challenges and difficulties in selecting reportable articles and news items, in writing, rewriting, and editing the selected articles, and in presenting timely editorials, all within the limited resources. This past year presented us with an additional challenge: When the Laboratory goes through one of the most challenging times as witnessed during the past year: when Los Alamos is in the national news almost daily with the disastrous Cerro Grande fire, the security breaches investigation, the Wen Ho Lee case, etc., it is extremely difficult for even the most scientific minded to focus on science and to ignore all the happenings around us as only unnecessary, irritating noises. An organizational newsletter is a living document so it suffers as do its authors and readers when things are not going well.

The past two or three years have been notoriously difficult for the coexistence between science and secrecy at the nation's nuclear Laboratories. For this situation my observations are

*Everywhere we look
Universe-full of wonders to the
students of science,
A world-full of secrets to the ever-
suspecting souls.*

*Everywhere we look
A limitless horizon of discovery
into the unknowns,
A countless number of opportuni-
ties for secrets to the jealous
souls.*

*Everywhere we look
A deep valley runs between the
world of science
And the proprietors of scientific
knowledge.*

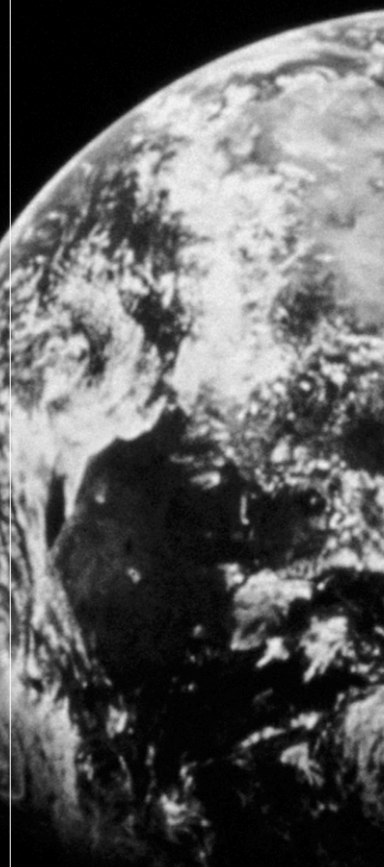
Readers of this newsletter may not have noticed any change of technical contents, but we have expanded the sources of our newsletter materials to include other technical organizations besides the NMT Division. We now rely upon continuing contributions of our broader actinide science community for the newsletter's articles. In this way we reaffirm the inter-relatedness of the actinide science community and highlight collaborations among various organizations and researchers.

The number of subscribers has increased more than three-fold over the six-year period although a "subscription" to this newsletter is only for the asking. We mail the newsletter worldwide, free of charge to individuals and organizations that request it. Once in a while, we receive praise and encouragement from a number of readers: One reader commented, "I have enjoyed *The Actinide Research Quarterly* very much, but the summer issue is special. The Seaborg article is superb, as it reminds us about the excitement of discovery." Another comments, "This good looking, quality newsletter is very informative." We received three awards of "Excellence in Technical Publications" from the New Mexico Kachina Chapter of the Society for Technical Communication along the way.

The newsletter also has served another important avenue of communicating scientific events worldwide. When the "Plutonium Futures-The Science" conference convened in Santa Fe in 1997 and 2000, *The Actinide Research Quarterly* was the main medium for us to publish the conference programs and also for reporting the main events of the conferences. There were 14 countries in the first conference and 15 countries in the second represented; our circulation of *The Actinide Research Quarterly* included all the participating countries.

ARQ is now on the Web also. Our readers can view entire back issues on-line <http://www.lanl.gov/orgs/nmt/nmtdo/AQarchive/AQhome/AQhome.html> Its Subject and author indexes are arranged.

Over time we, the publication team, realize how much we have learned just trying to keep up with the most current events in the actinide community, while we try to inform our readers. We find this to be one of the most rewarding aspects of publishing *The Actinide Research Quarterly*. In the end, every human endeavor is a learning process—publishing this newsletter is no exception. We draw immense satisfaction knowing that our readers and the publication team members have journeyed together the past six years on this learning path.



Recent Measurements Add to Understanding of Plutonium Metal's Electronic Structure

This article was contributed by **Roland Schulze** (NMT-16). Other researchers on the project are **J. Doug Farr**, **Jeff Terry**, and **Jeffrey Archuleta** (NMT-16); **John Joyce** and **Al Arko** (MST-10); **Jim Tobin** (LLN); and **David Shuh** and **Eli Rotenberg** (LBNL).

The electronic structure of a solid determines virtually all of its physical properties, excluding those nuclear in nature. It is extremely important to understand the character of the electrons near the Fermi energy (outermost) of the material because these electrons in particular are involved in bonding or conduction and collectively form the valence band of the solid. We have an ongoing effort to measure and understand the electronic structure of plutonium metal including all of its thermal allotropes (α , β , γ , δ , δ' , ϵ), and impurity-stabilized δ -plutonium. The methods we use include electron photoemission spectroscopy (PES), Auger electron spectroscopy, electron energy loss spectroscopy (EELS), and photon absorption techniques in the visible and x-ray regimes. This article describes the progress of our photoemission and EELS studies of Pu metal with the objective of understanding the electronic structure of this material and the unique changes it undergoes from low temperature to the liquid phase.

The methods we have used are in general sensitive only to the outermost surface (3 to 10 atomic layers) of the solid under investigation. Therefore, it is very important to understand the nature of the surface relative to the bulk of the material, in particular to insure that the surfaces are atomically clean. It is also necessary to distinguish the presence of possible surface reconfigurations that intrinsically alter the surface electronic structure from that of the bulk material. To that end, the sample preparation and spectroscopic measurements were made in an ultra high vacuum (UHV) environment ($\sim 10^{-10}$ Torr) in order to preserve the integrity of the surface for the duration of the measurements. Figure 1 shows the UHV Auger spectrometer/EELS instrument where some of these experimental measurements take place.

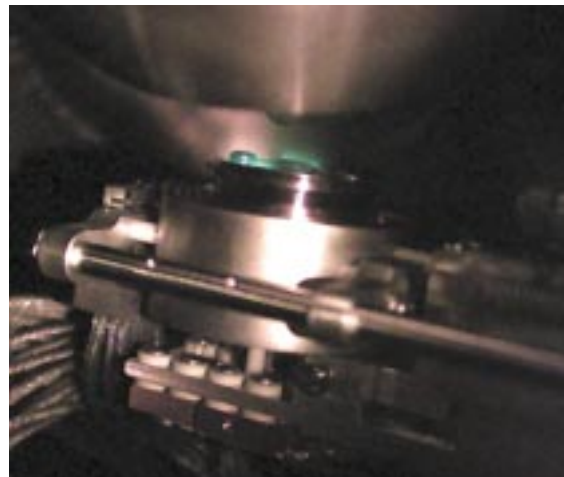


Figure 2. A pure plutonium sample in the UHV EELS instrument. The sample is mounted on a 1-inch puck, which sits in the hot/cold stage of the sample manipulator. The sample is illuminated by a green fluorescent glow in the early stages of ion sputter cleaning as a result of the presence of Pu oxide. The snout of the electron gun and the electron energy analyzer can be seen directly above the sample.

Figure 1. UHV scanning Auger spectroscopy/EELS instrument located in the Chemistry and Metallurgy Research building at Los Alamos. This instrument is used for fundamental actinide surface science research, plutonium physical properties measurements, and analytical surface characterization.



The electron energy loss measurements have shed light on two aspects of the plutonium metal allotropes: electronic reconfigurations at the surface of each allotrope, and changes in electronic environment induced through temperature changes of the pure Pu metal. We have made careful measurements of the EELS spectra from the surfaces of ion-sputter-cleaned and annealed Pu metal. An exhaustive number of sputter-cleaning and annealing cycles were required to attain a surface that was free of contamination (Figure 2). This effort resulted in a surface that would remain pristine, in the area of analysis, to less than 10% of a monolayer of oxygen impurity for a period of two hours, allowing us sufficient time to make high-quality measurements.

The EELS measurements involve bombardment of the Pu surface with 150 to 1000 eV electrons, with subsequent energy analysis of the scattered electrons. The scattered electrons have lost energy through interaction of the surface by a variety of different processes including excitation of plasmons (Figure 3) in the material, and promotion of electrons in atomic plutonium core levels to unoccupied states in the valence band of the solid. Plasmons are collective excitations of the electron gas (conduction electrons) in the material. Analysis of the plasmon response of the material over the range of primary electron energies that were used shows substantial changes as the depth of material sampled by the spectroscopy changes from approximately 8 to 18 Å. This behavior is consistent for each of the Pu thermal allotropic phases and the Ga-stabilized δ -Pu phase. This response indicates that the surface is being reconfigured in an electronic, and probably a structural nature, to an estimated depth of 10 Å (about 3 atomic layers) in each case. We believe that this reconfiguration involves a relaxation of atomic positions to something that is approximately a factor of three less dense atomically than the bulk structure. The precise nature of this reconfiguration is not yet understood.

In our measurements of plutonium, the intention is to obtain a value for the free electron count per atom in the solid and to examine how this value differs for each allotropic phase. In the case of EELS measurements at 700 eV primary electron energy, these measurements probe the electronic environment in the bulk (not surface layers) of the Pu metal. We observe up to three bulk plasmon loss events spectroscopically, with peaks evident at approximately 11, 22, and 33 eV loss energy. A compilation of the 700 eV EELS spectra for each thermal allotrope exhibits subtle shifts in the energy of the plasmon resonance peaks as a result of changes in the free electron volume density with the allotrope.

The bulk plasmon resonance energy is used to extract the free electron volume density. The free electron count per atom is calculated by correcting the volume density using the atomic volume density specific for each allotrope. The free electron count per atom appears to be nearly invariant over the range of allotropes, but the subtle changes, however, track exactly with changes in other measured physical properties such as absolute resistivity and magnetic susceptibility. This pattern indicates that the changes in the free electron density measured here are identically responsible for these changes in electronic properties over the allotropic series. These changes, however, do not reflect the traditional view of a shift in 5*f* electron nature from itinerant to localized with increasing temperature across the allotropic series. Alternatively, the measurements made with this technique probe free electron behavior not associated with the Pu 5*f* valence electrons, suggesting that the 5*f* electrons largely do not participate in charge conduction or magnetic properties of Pu. Future measurements and ongoing analysis may clarify these details.

Our photoemission measurements probe the occupied density of states (DOS) in the plutonium and include core level states as well as valence band states (see also Actinide Quarterly, first quarter 1999). This measurement involves absorption of an x-ray or ultraviolet photon by an atom in the solid with corresponding ejection of a photoelectron from the surface of the material.

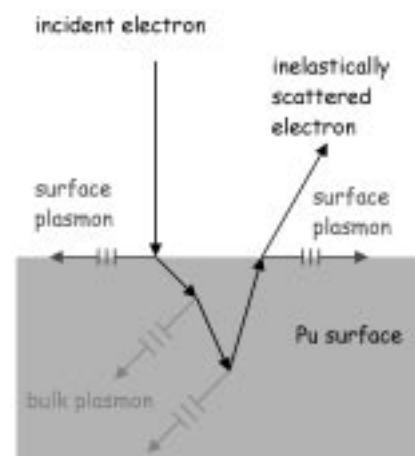


Figure 3. Schematic representation of an incident primary electron undergoing energy losses due to excitation of plasmons. In the general case the electron may lose energy by exciting a surface plasmon upon entering and exiting the solid (maximum of 2 surface plasmon excitations possible), and may lose energy by exciting any integral number of bulk plasmon losses.

Recent Measurements Add to Understanding of Pu Metal's Electronic Structure (*continued*)

Through an energy balance, the binding energy of the electron in the solid (as part of the electronic density of states) is related to the measured kinetic energy of the photoelectron and the original photon energy. This is the first step in mapping out the electronic structure of Pu metal, with an ultimate goal of measuring the band structure of each allotrope. In this way we hope to understand the electronic band structure changes that plutonium undergoes with each thermal phase transformation, as well as the electronic mechanism for impurity stabilization of the δ -Pu phase. In addition, the unoccupied density of states above the Fermi energy can be examined through the use of near edge x-ray absorption fine structure (NEXAFS) and inner shell EELS (ISEELS) measurements. These are analogous processes in which a core-level electron is promoted into an unoccupied state through absorption of a photon (NEXAFS) or through an inelastic energy loss of a primary electron in the EELS measurements. To a first approximation, within the constraints of the orbital selection rule, the spectroscopic shape of the absorption curve or the loss feature is a convolution of the narrow core level and the shape of the unoccupied states. Thus as shown in Figure 4, we have been able to assemble a complete experimental representation of the electronic density of states from the atomic core levels to the occupied and unoccupied states of the solid valence band.

Fundamental studies involving photon and electron interactions with plutonium surfaces continue in our laboratories in an attempt to understand the electronic structure of the metal. An understanding is of paramount importance with regard to the electronic contribution to changes in crystal structure and physical properties with thermal phase changes in plutonium metal, and the nature of the impurity stabilization of the δ -Pu phase. An accurate description will help us to understand materials stability, solid-state reactions, and surface chemistry of plutonium metal.

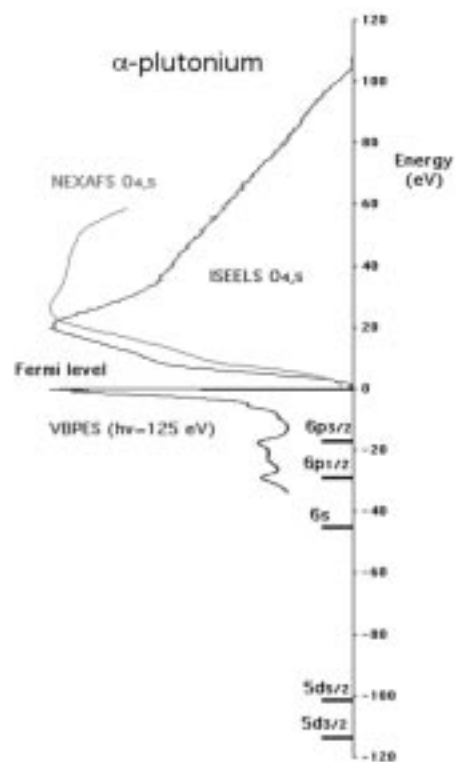


Figure 4. Experimental electronic structure DOS representation for α -plutonium metal. The occupied valence band DOS was probed by valence band photoemission spectroscopy (VB PES), and the unoccupied DOS was probed by NEXAFS and ISEELS measurements. Some of the deeper core levels below the Pu 6s state are accessible using soft x-ray photoemission (experimental spectrum not shown).

Publications and Invited Talks (December 1999—December 2000)

If you are the author of a *published* paper (book, book chapter) or an *invited* talk, please e-mail the particulars to mauzy@lanl.gov.

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Fife, K.W., J. L. Alwin, C. A. Smith, M. D. Mayne, and D. A. Rockstraw, "Vitrified Magnesia Dissolution and Its Impact on Plutonium Residue Processing," Los Alamos National Laboratory report LA-13680-MS (March 2000).

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Newsmakers

■ **Award:** The NMT-9 team responsible for supplying heat sources to the Galileo mission was recently awarded the National Space Club's Nelson P. Jackson Aerospace Award for outstanding contribution to planetary exploration. Team members are **Roy Zocher, Tim George, Gary Rinehart, Theresa Cull, and Art Herrera.**

■ **Pollution Prevention Award:** **Bob Grundemann** and **Susan Ramsey** of Power Source Technology (NMT-9) and **Scott Ferrara** of the Idaho National Engineering and Environmental Laboratory won a Pollution Prevention Award this year for improvements they made to the plutonium residue solidification process.

■ **New Division Review Committee member:** Dr. William (Bill) F. Weston, (Boeing Company, Rocketdyne Division), has agreed to serve as a member of the Division Review Committee. The next review is planned for May 8–11, 2001. The committee will accomplish the work of the review that was scheduled for May 2000 but was postponed as a result of the Cerro Grande fire. Weston joins Dr. Richard A. Bartsch (Texas Tech University), Dr. Rohinton K. Bhada, Dr. Darleane C. Hoffman (Lawrence Berkeley National Laboratory), Dr. Todd R. LaPorte (University of California, Berkeley), Dr. W. Lamar Miler (University of Florida, Consultant), Dr. Anthony (Tony) D. Rollet (Carnegie Mellon University), Dr. Ned A. Wogman (Battelle, Pacific Northwest Laboratories, Consultant), and Dr. Susan Wood (Westinghouse Savannah River Company, Committee Chair).

■ **New SLC Members:** Eleven NMT scientists and engineers were nominated for this year's selection of the Science Leadership Council in NMT, and five have been selected. SLC members are all accomplished senior scientists within NMT who have demonstrated significant scientific and technical achievements and hold peer recognition, external reputation, and visibility in their respective scientific and technical fields. All non-managers, the SLC is charged with providing leadership in directing the division's efforts in scientific and technical research. The newly selected members are **Gary Eller, Laura Worl, Robert Margevicius, Ed Garcia, and John Park.**

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