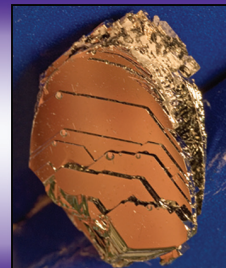
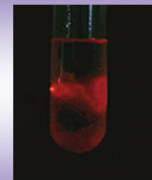
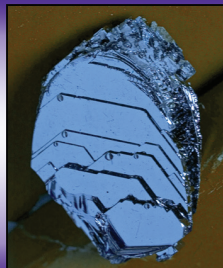
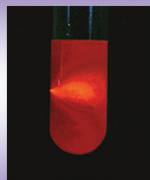
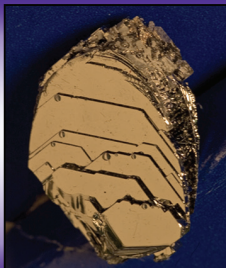
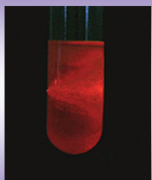
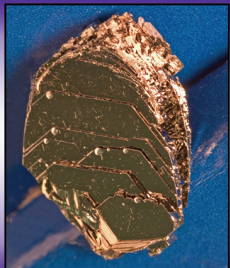




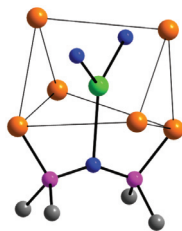
Los Alamos National Laboratory  
**ACTINIDE RESEARCH  
QUARTERLY**

2nd quarter 2005

**Postdoctoral research programs  
fuel the research engine**

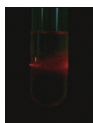




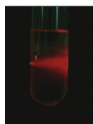


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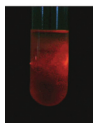
ACTINIDE RESEARCH QUARTERLY



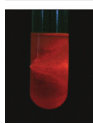
**1 Postdoctoral research programs fuel the research engine and recruit new talent**



**3 Preparation of sulfur and selenium donor complexes advances actinide science and separations**

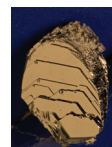
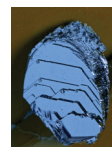


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## Postdoctoral research programs fuel the research engine and recruit new talent

The core mission of the NNSA and its Laboratories is to enhance global security by ensuring confidence in the safety, reliability, and performance of U.S. nuclear weapons without testing; develop technical solutions to reduce the threat of weapons of mass destruction; and improve the environmental and nuclear materials legacy of the Cold War. However, no national security program can be better than the quality of the scientists and engineers doing the work and providing the necessary leadership. Of grave concern is that a large percentage of Los Alamos staff has recently retired, or will retire within the next year and the coming decade.

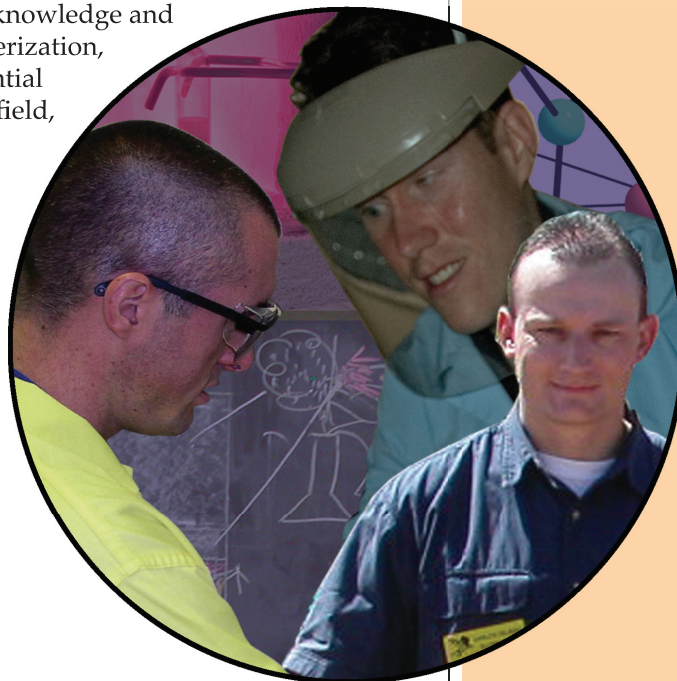
The Laboratory's postdoctoral fellows programs provide one key mechanism by which Los Alamos attracts the next generation of scientists and engineers. Recruiting statistics reveal that an impressive 55 percent of new Technical Staff Members hired in 2004 first joined the Laboratory as postdoctoral fellows. This striking statistic illustrates that postdoctoral fellows programs play a significant role in recruiting new talent to the Laboratory.

Postdocs generally don't come to the Laboratory to work for the Laboratory per se; instead they are attracted to the Laboratory by a cadre of prominent scientists and engineers who are actively publishing exciting new science in the world's most prestigious scientific journals. This is one reason why it is so important for the Laboratory to foster great science and to help our scientists and engineers sustain visible excellence in relevant scientific areas. This is particularly true in the area of actinide science, which is crucial to the core weapons, nonproliferation, and environmental missions of the Laboratory.

Actinides are the large group of elements ranging from thorium through lawrencium, and include the elements uranium and plutonium. Knowledge of actinide science continues to be essential to the United States and central to the mission of the NNSA, including national defense, homeland security, energy, environmental restoration, and radioactive waste management. With nuclear weapons technology continuing to play a key role in defense policy for the foreseeable future, and with emerging threats of radiological terrorism, knowledge and expertise in the production, processing, purification, characterization, analysis, detection, and disposal of actinide elements is essential to U.S. national security. We worry about retirements in this field, and we have the added reality that the academic component of this field is small and decreasing. As faculty in actinide science-related fields retire, they are often not replaced because of the high cost, negative public perception, and the general risk associated with handling and disposing of radioactive materials.

Because of concern that the field is becoming subcritical at a time when this core competence is crucial for U.S. national security, it is strategically important for the Laboratory to increase its investment in actinide science education. In response to this need, the Los Alamos branch of the Seaborg Institute has sponsored an actinide science summer school, with formal courses and hands-on laboratory experiences for students, and a Summer Lecture Series for all Laboratory personnel.

*Postdocs Andrew Gaunt, Eric Bauer, and Ralph Zehnder write about their research and experiences in this issue of ARQ.*





## POSTDOCTORAL RESEARCH PROGRAMS

This year we launched a new Seaborg Institute Postdoctoral Fellows Program for education and training, and for assisting the Laboratory with recruiting a pool of highly talented postdocs in actinide science fields. We are proud to highlight the scientific research and educational outreach activities of three of our postdocs in this issue of *Actinide Research Quarterly*.

In the first article by Andrew Gaunt from Chemistry Division, we learn of fundamental new chemistry displayed by actinide elements interacting with “soft” electron donor atoms such as sulfur and selenium. These soft-donor complexes are important in advanced nuclear fuel cycles because they can accomplish the efficient solution separation of trivalent actinides from trivalent lanthanides. It is generally believed that this separation is achieved because of greater covalency in metal-ligand bonding in actinides relative to lanthanides. Andrew’s work will go a long way toward helping us understand the nature of metal-sulfur and metal-selenium bonding, and ultimately understand the factors that lead to enhanced covalency in actinides relative to lanthanides.

The next article features the work of Eric Bauer from Materials Science and Technology Division, one of the first postdoctoral fellows sponsored by the Seaborg Institute’s new program. Eric has recently been named the Laboratory’s second Frederick Reines Fellow. Eric and his colleagues describe new ways to modify and enhance a rather exotic superconductivity in a new class of plutonium intermetallic compounds. We learn that superconductivity in these intermetallics is associated with the tendency of the 5f electrons to display both localized and itinerant behavior. Eric’s work reveals that the plutonium superconductivity is unconventional, and that a layered two-dimensional structure likely imparts some

control over spin fluctuations of the 5f electrons. The 5f electron behavior shows some similarity to the 5f behavior in delta-stabilized plutonium. What we learn from studies of plutonium superconductivity will likely help us to understand the enigmatic nature of plutonium metal itself.

The final article is written by Ralph Zehnder from Chemistry Division, who has finished postdoctoral studies and will begin his tenure as an assistant professor of chemistry at the University of Louisiana this fall. Ralph’s research has been in the area of solid-state f-element chemistry, but this is not the topic of his contribution. Instead, Ralph shares an inspiring story about community outreach that reminds us of the tremendous impact that good teachers can have on the lives of young students. Ralph’s account of his interaction with grade-school children reminds us that as Los Alamos scientists and engineers, we are also members of a larger community—a community full of children ready and eager to learn about the natural world. With only a small investment of time, Los Alamos scientists and engineers can help explain this natural world to children in northern New Mexico, and perhaps set some on the path to become scientific leaders of the future.

Postdoctoral programs at Los Alamos offer the opportunity for young investigators to perform research in a scientifically rich environment, present and publish research, contribute to the overall research efforts at the Laboratory, advance knowledge in the areas of basic and applied research, and strengthen our national scientific and technical capabilities. Postdoctoral programs are one of the most successful recruiting tools at the Laboratory. For more information on postdoctoral programs at Los Alamos, see <http://www.lanl.gov/science/postdocs/>.

—David L. Clark and Gordon D. Jarvinen,  
ARQ Scientific Advisors



*Illuminating the nature of f-element bonding with 'soft' ligands*

## Preparation of sulfur and selenium donor complexes advances actinide science and separations

An intimate knowledge of the fundamental coordination chemistry of the actinides is vital to understanding processes and separations for the minimization and treatment of nuclear waste. One possible strategy to reduce the volume and storage time of high-level waste is partitioning and transmutation. In this approach the long-lived minor actinide isotopes are placed in a reactor and subjected to a neutron flux causing them to be transmuted via nuclear reactions to isotopes with shorter half-lives, which decreases storage costs.

Before transmutation, it is crucial to separate the trivalent actinides, referred to here as An(III), from trivalent lanthanides, Ln(III), because some of the lanthanides are "neutron poisons" and the amount of material put through the reactor should be minimized. The separation of An(III) and Ln(III) is particularly difficult because the generally ionic nature of the bonding for "hard" metal ions means many extractants display no selectivity between An(III) and Ln(III) of similar ionic radii, such as americium(III) and europium(III).

However, the sulfur-bearing Cyanex extractants (dithiophosphinic acids, which have a negative charge delocalized over two sulfur atoms) display an exceptional preference for An(III) over Ln(III). Conclusive experimental evidence for the origin of this preference is lacking. The prevailing theory is that because sulfur is a "softer" (less electronegative), more polarizable donor atom, subtle differences in covalent contributions to the bonding may provide selectivity.

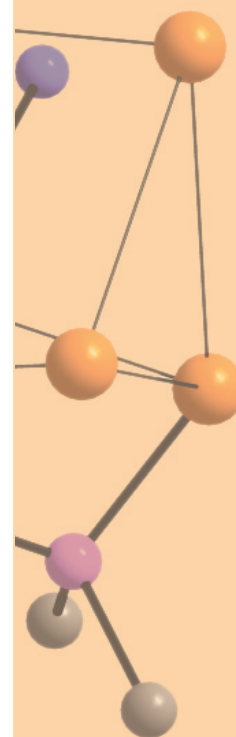
The rationale for this hypothesis is that relativistic effects are more pronounced for the actinides than for the lanthanides. Consequently, the 6d and 5f orbitals of An(III) are more spatially diffuse than the 5d and 4f orbitals of Ln(III) of similar ionic radii. Therefore, there exists potential for greater overlap (covalency) between the metal and ligand orbitals for the actinides than for the lanthanides. The difference in energies of the valence orbitals between the trivalent actinides and lanthanides in relation to the valence ligand orbitals also contributes to actinide-ligand interactions.

Despite the importance of actinide and lanthanide separations, relatively few research efforts have focused on understanding the extraction behavior of Cyanex reagents from a coordination chemistry perspective; one of our key objectives is to help fill this gap in knowledge. Historically, studies of covalency in actinide bonding use complexes in which most of the coordination sites are occupied by sterically demanding functionalities to focus covalency toward one or two metal-ligand bonds.

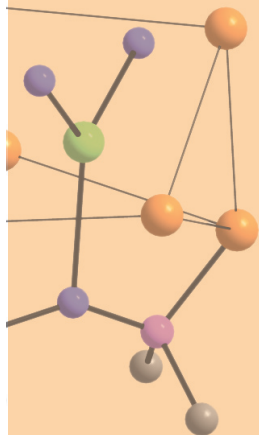
Our research has a slightly more applied flavor in the sense that we are synthesizing homoleptic compounds (i.e., the entire actinide

This article was contributed by Andrew J. Gaunt, Brian L. Scott, and Mary P. Neu of the Actinide, Catalysis, and Separations Chemistry Group (C-SIC).

Photos by  
Mick Greenbank



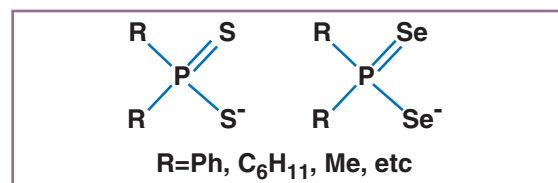


ACTINIDE  
COORDINATION  
CHEMISTRY

coordination sphere is available for bonding by the same ligand) with nitrogen (N), sulfur (S), and selenium (Se) donor atoms, providing coordination environments relevant to An(III) and Ln(III) separations. By taking a systematic approach to synthesizing actinide complexes with ligands of differing electronegativities, or softnesses, and comparing these complexes with related lanthanide complexes, we aim to determine a structural and coordination basis for preferences in such complexes and assess subtle differences in the bonding between the 5f and 4f elements.

### Syntheses of soft-donor actinide complexes

In pursuing the isolation of molecular compounds containing actinide-chalcogen bonds, we have chosen a broad range of ligands bearing nitrogen, sulfur, and selenium donor atoms, including dithiophosphinates, diselenophosphinates, thiolates, selenolates, and imidodiphosphinochalcogenides. We have also identified synthetic pathways to the corresponding actinide complexes. Given the notable preference of dithiophosphinic acids for An(III) over Ln(III), a logical class of compounds to target are derivatives of the Cyanex extractant. To modify the solubility and physical properties of the ligand, while maintaining the metal-chelate characteristics, the long hydrocarbon chains of the Cyanex extractant are replaced with groups to aid crystallization. To expand the basis for comparisons, either

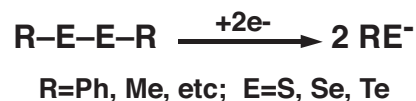


*Dithiophosphinates (left) and diselenophosphinates (right) are crystallizable derivatives of Cyanex extractants, which can be used to study fundamental coordination chemistry.*

sulfur or selenium can be incorporated as the donor atom to vary the softness of the ligand.

Thiolates and selenolates are another class of sulfur and selenium donor ligands. Work by John G. Brennan and others at Rutgers, the State University of New Jersey, has demonstrated that elemental lanthanides can be oxidized by dichalcogenides. Using a similar methodology, uranium metal can be oxidized by reductive cleavage of a chalcogen-chalcogen bond to form thiolates and selenolate anions that complex to the uranium metal center.

Imidodiphosphinochalcogenides are mixed N, E (E = S, Se) donor ligands that can be considered softer than, for example,  $\text{PhE}^-$  because the negative charge is delocalized, whereas for  $\text{PhE}^-$  the negative charge is localized on a single



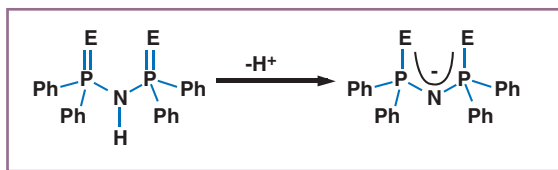
*Scheme showing reductive cleavage of the bond in dichalcogenides to form anionic thiolate and selenolate ligands. The electrons are provided by uranium metal ( $\text{U}^0$ ) oxidized with concomitant solubilization during the process.*

chalcogen atom. The rest of this article will focus on uranium complexes with this class of ligands and highlight how they are providing insight into actinide structure and bonding.

### Uranium(III) imidodiphosphino-sulfide and -selenide complexes

The chemistry of the actinides with anionic ligands of general formula  $[\text{N}(\text{EPPH}_2)_2]^-$  (E = S, Se, Te) is completely unexplored, yet they offer a facile entry into the synthesis of low-valent 5f complexes with the chalcogens as donor atoms. The homoleptic, trivalent uranium complexes,  $\text{U}[\text{N}(\text{SPPH}_2)_2]_3$  (1) and  $\text{U}[\text{N}(\text{SePPH}_2)_2]_3$  (2), have been isolated by treating  $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$  with three equivalents





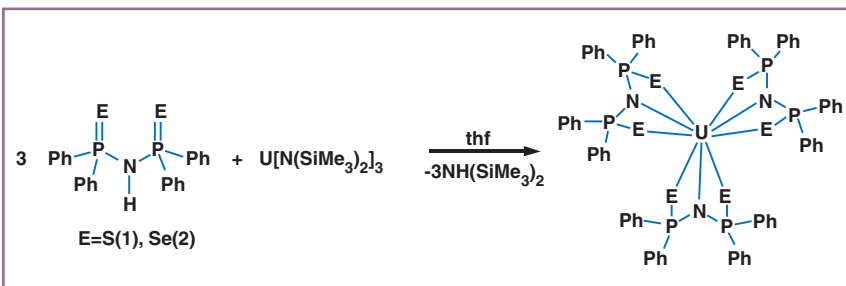
Deprotonation of the nitrogen atom results in an anionic ligand with the negative charge delocalized over the [EPNPE] moiety ( $E = S$  or  $Se$ ).

of  $NH(SPPH_2)_2$  and  $NH(SePPh_2)_2$ , respectively. Single crystals of **1** and **2** can be grown from a THF/toluene solvent mixture.

The X-ray crystal structures of **1** and **2** are isomorphous. In these complexes the uranium(III) center is nine-coordinate and adopts a distorted tricapped trigonal prismatic geometry. Each of the three ligands is tridentate, binding to uranium through both the chalcogen atoms and the nitrogen atom. The U-S distance in **1** is 2.9956(5) angstroms

3.1234(4) Å, slightly longer than the U(III)-Se distance in **2** by 0.0365 Å. The ionic radii of U(III) and La(III) differ by only 0.005 Å; therefore, the difference in U-Se and La-Se bond lengths is significant and is consistent with U(III) having slightly more affinity for soft-donor atoms than does La(III).

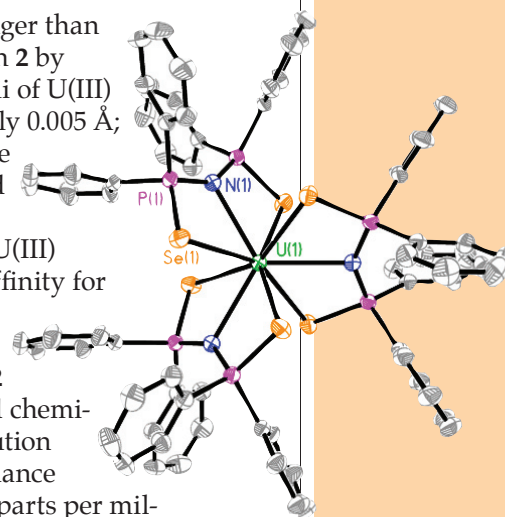
Compounds **1** and **2** both display high-field chemical shifts in the  $^{31}P$  solution nuclear magnetic resonance (NMR) spectra at -681 parts per million (ppm) for **1** and -723 ppm for **2**. A variable temperature  $^{31}P$  NMR study of the complexes reveals the expected temperature dependence of about 250 ppm over the temperature range 10 to -50 degrees Celsius. The solution electronic absorption spectra of **1** and **2** reveal distinctive U(III) Laporte-forbidden 5f-5f transitions in the 750 to 1,300 nanometer (nm) region, with more intense bands



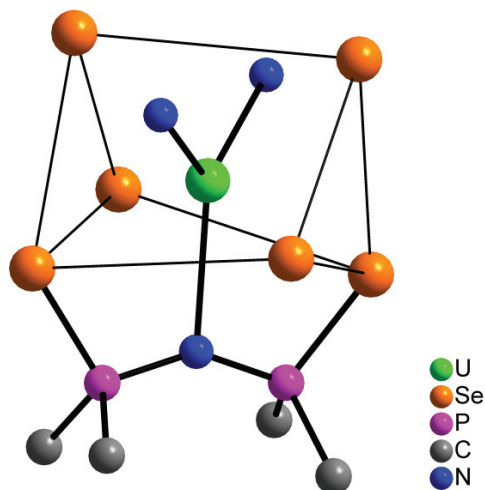
Reaction scheme of the synthesis of  $U[N(SPPH_2)_2]_3$  and  $U[N(SePPh_2)_2]_3$ .

(Å) compared to the expected longer distance of 3.0869(4) Å for U-Se in **2**. The U-Se bonds are the first examples of crystallographically determined An(III)-Se bonds in molecular complexes, reflecting the challenge associated with preparing such compounds and the paucity of knowledge in the area of actinide-chalcogen bonding.

Indeed, only fairly recently have molecular U(III)-S bonds been structurally determined. Complex **2** can be compared to  $Cp_2La[N(SePPh_2)_2]_3$ , in which the lanthanum(III)-Se distance is

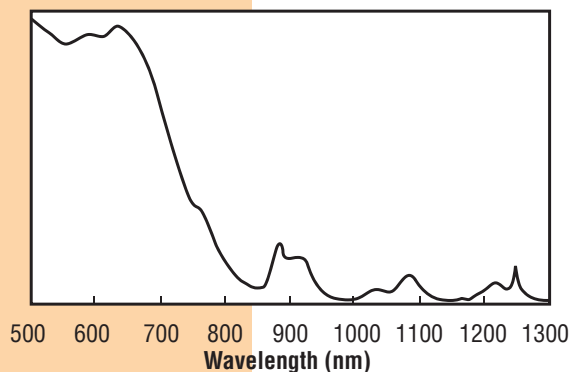


The thermal ellipsoid representation (above) of the crystal structure of compound **2** shows the tridentate ligating nature of the anions. The U-Se bonds are the first examples of a structurally characterized An(III)-Se bond in a molecular complex. The ball-and-stick diagram (below left) displays the distorted tricapped trigonal prismatic coordination geometry of the U(III) ion (only the inner sphere atoms and part of one ligand are shown; the rest have been omitted for clarity).



● U  
● Se  
● P  
● C  
● N

## ACTINIDE COORDINATION CHEMISTRY



The UV-vis spectrum (above) of  $U[N(\text{SePPh}_2)_2]_3$  (**2**), in benzene solution displays the 5f-5f and 5f-6d transitions of U(III), which is isolated as a gray/brown powder in the solid state (below).



in the 550 to 700 nm region attributed to Laporte-allowed 5f-6d transitions.

This work opens up a new area of study in actinide chemistry in the preparation of a series of discrete actinide-chalcogen complexes with

particular emphasis on comparison of isostructural An(III) and Ln(III) complexes of similar ionic radii to examine for subtle differences in the nature of the bonding. Initial results support the hypothesis that An(III) ions have a stronger interaction than Ln(III) ions for ligands bearing softer donor atoms.

### Future directions

We are preparing a series of uranium compounds with nitrogen, sulfur, and selenium donor atoms. The characterization of these complexes, which contain only uranium-chalcogen bonds and solvent molecules in the inner coordination sphere, will greatly enhance our understanding of structural preferences and bonding types in these systems. In addition to the characterization techniques described in this article, future studies will include X-ray photoelectron spectroscopy to probe the energies of the molecular orbitals involved in bonding and ligand-metal orbital interactions.

We are also measuring the magnetic properties of the compounds to better quantify the delocalization of the electrons away from the actinide ion. As the number of complexes synthesized increases and more comparisons to lanthanides are drawn, we may see a trend emerge from which subtle differences between actinide and lanthanide bonding with soft-donor ligands can be elucidated.



The preparation of An(III) and (IV) complexes with “soft” donor atom ligands requires inert atmosphere techniques such as the use of this helium-filled glovebox at the Actinide Research Facility at TA-48. The glovebox is maintained at a pressure slightly negative relative to atmospheric pressure, the inlets/outlets are HEPA filtered, and the antechamber opens directly into a HEPA-filtered fume hood. This configuration allows transuranic isotopes such as plutonium-239 to be safely handled and manipulated. Seaborg postdoctoral researcher Andrew Gaunt cogitates over a reaction (inset).

A principal component of future research will focus on extending this chemistry to plutonium(III). Because of the actinide contraction, trivalent plutonium is more stable, with respect to oxidation, than trivalent uranium and therefore is attractive to use for the study and comparison of An(III) and Ln(III) complexes with soft-donor atom ligands. In addition, very few coordination chemistry studies and structural characterizations have been conducted for the transuranic elements because the high specific activity renders their manipulation challenging and requires specialist radiological facilities. For this reason, the isolation of Pu(III) complexes with soft donors will not only contribute to a general picture of 5f element bonding but will also offer a unique insight into the chemistry of this fascinating, yet inadequately understood, element.



## Researchers find two simple but elegant ways to enhance superconductivity Tuning plutonium superconductors

Following the exciting discovery of superconductivity in plutonium-cobalt-pentagallium ( $\text{PuCoGa}_5$ ) by Los Alamos' John Sarrao, Joe Thompson, and Luis Morales, scientists around the world quickly attempted to capitalize on this breakthrough by searching for superconductivity in other relatives of the same family of materials. Shortly thereafter, superconductivity was reported in  $\text{PuRhGa}_5$  by Franck Wastin and collaborators at the Institute for Transuranic Elements in Karlsruhe, Germany.

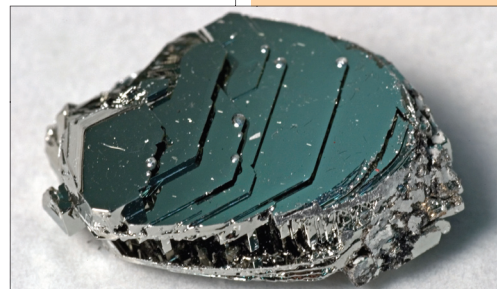
While the superconducting transition temperature  $T_c$  of  $\text{PuRhGa}_5$  is half that of  $\text{PuCoGa}_5$  (8.7 kelvin (K) compared with 18.5 K, respectively), superconductivity in these two compounds is nearly an order of magnitude higher than all other known actinide superconductors, such as  $\text{UPt}_3$  and  $\text{UBe}_{13}$  discovered at Los Alamos in the 1980s by Zachary Fisk and Jim Smith. There are indications that this dramatic enhancement of the superconducting properties of these plutonium-based materials may stem from the "dual-nature" of the plutonium 5f electrons. (For a general introduction to the physical properties of elemental plutonium, see the article by A. Michael Boring and James L. Smith, *Los Alamos Science* No. 26, 2000. For more on the superconductivity of  $\text{PuCoGa}_5$ , see *Actinide Research Quarterly* 3<sup>rd</sup>/4<sup>th</sup> Quarter, 2002.)

Characteristics of localized behavior, where the f electrons carry magnetic moments and are contained within their atomic shells, and also behavior associated with itinerant f electrons in which they leach out and mingle with the conduction electrons that are free to move about the crystal, are manifest in  $\text{PuMGa}_5$  (M = cobalt, rhodium). Because the 5f electrons of plutonium appear to be poised at the boundary between localization and itinerancy, a situation well known to exist in the various crystallographic phases of elemental plutonium, the  $\text{PuMGa}_5$  materials may shed new light on the complicated electronic structure of plutonium.

On their quest to unravel the complex nature of the plutonium f electrons in these two intermetallic compounds, scientists at Los Alamos have found two rather simple but elegant ways to enhance the superconductivity in these materials. The first way involves a very slight stretching of the tetragonal crystal structure of  $\text{PuMGa}_5$  along the longest dimension culminating in a linear increase in the superconducting transition temperature with the ratio of the lattice parameters  $c/a$ . Remarkably, such a sensitive structural tuning of superconductivity is also found in the  $\text{CeMIn}_5$  (M = cobalt, rhodium, iridium) heavy-fermion superconductors that belong to the same "115" family. (These new crystalline materials are composed of three different elements in the ratio 1:1:5; hence the term "115.")

A wealth of theoretical and experimental work on structural tuning in other layered materials (the high- $T_c$  cuprate superconductors are a classic example) indicates that superconductivity in these plutonium- and cerium-based materials might be more exotic than the simple, garden-variety kind found in many elements in which the "glue" that binds superconducting electrons into pairs is made of jiggling atoms, or lattice vibrations. Instead, the glue that holds the superconducting electrons together in this more unusual (or unconventional) form of superconductivity may be comprised of magnetic excitations.

While there were hints of exotic superconductivity in  $\text{PuCoGa}_5$  in the early work (already well established in the  $\text{CeMIn}_5$  compounds), conclusive evidence was not available until Nicholas Curro and Tod Caldwell measured the nuclear magnetic resonance (NMR) of the cobalt and gallium nuclei. These researchers showed that the temperature



*This large single crystal of  $\text{CeMIn}_5$  was prepared by the molten-metal flux technique. The elements were put into an alumina crucible with excess indium, a low-melting point metal (flux) that acts as a solute (similar to growing sugar crystals out of a sugar-water mixture), and sealed under vacuum in a quartz tube. The mixture was heated above its melting point, then cooled slowly to a temperature where the flux is still molten. A centrifuge was used to separate the single crystals from the molten flux. The colors of the crystal shown above and on the front and inside covers were enhanced with a filter.*

Photos by  
Mick Greenbank

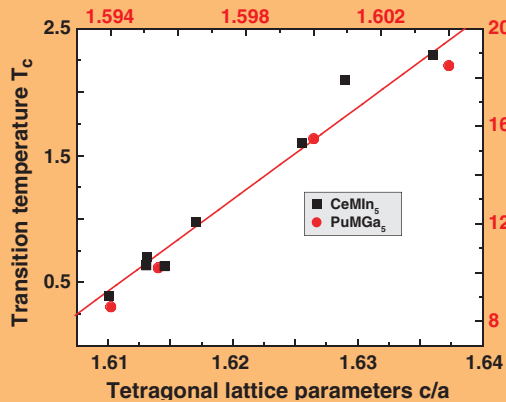
PLUTONIUM  
SUPER-  
CONDUCTORS

dependence of the physical properties in the superconducting state followed that expected for an unconventional superconductor.

Quite unexpectedly, the NMR results,

which appeared in the March 31, 2005, issue of *Nature*, also revealed a characteristic energy scale for the magnetic excitations mediating the superconductivity in the plutonium materials that is intermediate between values known in two other classes of unconventional superconductors, the heavy-fermions and the high- $T_c$  cuprates. Thus, tuning the magnetic excitation spectrum provides another way to enhance superconductivity in these compounds. The establishment of a continuum of energy scales within this mechanism of superconductivity that are directly proportional to the superconducting transition temperature supports a long-cherished belief that heavy-fermion and high- $T_c$  cuprate superconductors are intimately related.

Enhancing superconductivity

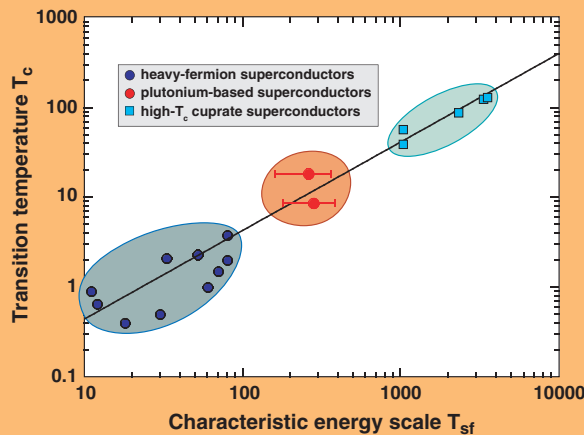


The striking similarity between the CeMn<sub>5</sub> (M = cobalt, rhodium, iridium) and PuMGa<sub>5</sub> (M = cobalt, rhodium) superconductors was one of the first indications that the superconductivity observed in the plutonium materials might be unconventional. In both families of superconductors, a very small increase in the anisotropy of the tetragonal lattice parameters  $c/a$  results

in a factor of two to three increase in the superconducting transition temperature. The nearly identical relative slopes of the linear increase of  $T_c$  with  $c/a$  indicates that the cerium- and plutonium-based superconductors share common physics: namely, that the unconventional superconductivity is structurally tuned quite effectively.

Another way to enhance the superconductivity in the heavy fermion materials is exemplified by the PuMGa<sub>5</sub> (M = Co, Rh) compounds. By increasing the characteristic energy scale of the spin fluctuations in PuMGa<sub>5</sub> relative to CeMn<sub>5</sub> (M = Co, Rh, Ir), the superconducting transition temperature increases correspondingly in a linear manner. The values of the characteristic energy scale and  $T_c$  of the plutonium superconductors places them in the gulf that once stood between the

heavy-fermion and high- $T_c$  cuprate superconductors. It is now clear that a continuum of energy scales present in these unconventional superconductors leads to ever-increasing values of superconducting transition temperatures.



Magnetically mediated  
superconductivity

While various initial measurements hinted at exotic superconductivity in the plutonium-based compounds, the real proof came from nuclear magnetic resonance measurements performed by Curro and Caldwell on single crystals of PuCoGa<sub>5</sub> prepared by Morales, Sarrao, and Eric Bauer. The Knight shift of the cobalt and gallium nuclei, which is sensitive to the spin symmetry of the superconducting order parameter, and the power law temperature dependence of the spin lattice relaxation rate  $T_1^{-1}$ , which probes the low-energy excitations allowed by the orbital symmetry of the paired electrons, provided strong evidence for just the kind of superconductivity expected with a spin fluctuation glue.

It turns out that spin fluctuations constrained to propagate in two dimensions enhance superconductivity to a much greater extent than their three-dimensional counterparts. This likely is the reason that unconventional superconductivity is most often found in materials with layered two-dimensional structural units; examples include the "CeIn<sub>3</sub>" layers in CeMn<sub>5</sub> and the copper-oxide planes in the high- $T_c$  cuprates. Therefore, any structural tuning of



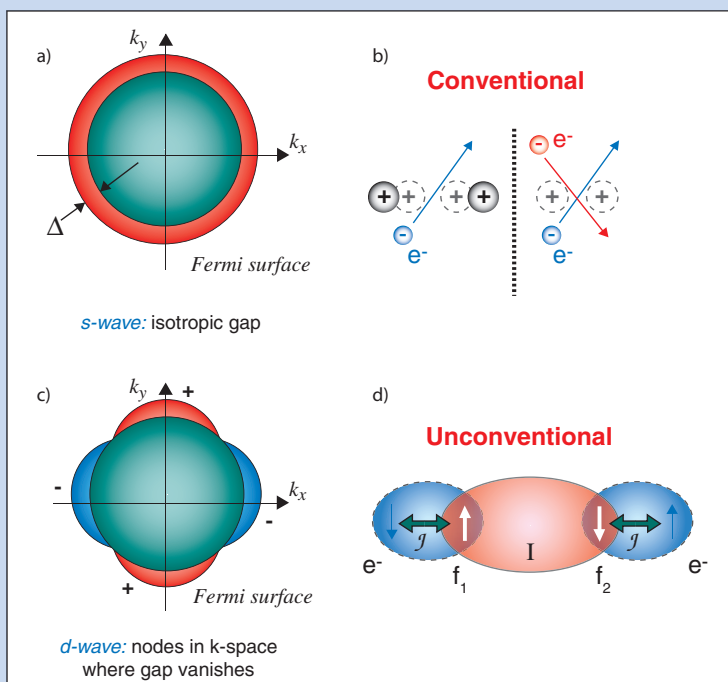
these layers should drastically affect the relevant spin fluctuations responsible for the unconventional superconductivity. This is precisely what is believed to lead to the striking linear relation between the ratio of tetragonal lattice parameters  $c/a$  and superconducting transition temperature  $T_c$  in the  $\text{CeMIn}_5$  and  $\text{PuMGa}_5$  compounds.

Further support for magnetically mediated superconductivity in  $\text{PuCoGa}_5$  has come from theoretical calculations carried out by Los Alamos researchers Matthias Graf and Sasha Balatsky and by Y. Bang at Chonnam National University in South Korea. Their calculations were able to self-consistently account for a decrease in the superconducting transition temperature with time and for the effects of the radiation damage of plutonium in the NMR data, making both the superconductivity and predictive theory invaluable tools for investigating the effects of aging in plutonium, a relevant

## Mechanisms of superconductivity

### Conventional phonon (lattice vibration) mediated superconductivity

In a conventional superconductor described by the now famous theory of Bardeen, Cooper, and Schrieffer, the free electrons form Cooper pairs with opposite spin and momenta due to an attractive interaction mediated by lattice vibrations (phonons). Below the critical temperature  $T_c$ , these Cooper pairs undergo a macroscopic condensation to a quantum state with net zero angular momentum and spin that is separated from other possible electron states by a finite energy gap  $\Delta$  (a). Experiments that probe the density of electron states, such as specific heat and spin lattice relaxation rate, exhibit activated behavior (exponential temperature dependence) at low temperatures.



A simple picture of how lattice vibrations lead to an attractive interaction between two electrons is shown in panel (b). One conduction electron moving through the solid polarizes the positive ions around it. A second electron in the vicinity at a slightly later time will be attracted to the net positive polarization caused by the first electron.

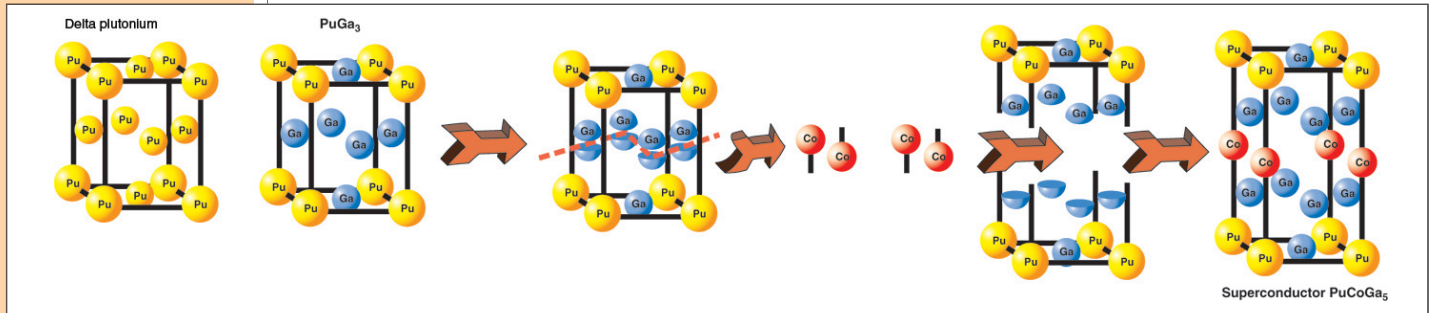
### Unconventional magnetically (spin fluctuation) mediated superconductivity

Life gets much more interesting (and somewhat more complicated) in the presence of very strong electron-electron interactions, a hallmark of both the heavy-fermion and high- $T_c$  copper oxide superconductors. Strong Coulomb interactions, which compete with the attractive phonon mediated interaction, and the robust magnetism found in these sorts of systems, which scatter and break the Cooper pairs rather effectively, tend to preclude such a lattice-mediated mechanism of superconductivity. The material may then seek a more exotic route to this lowest energy macroscopic quantum state; the simplest and most appealing way to the superconducting state is to choose a Cooper-pair glue made from low-energy antiferromagnetic magnetic excitations, or spin fluctuations.

In this unconventional type of superconductivity, some form of electron pairing still occurs, but now the pairs have more freedom for their spin and angular momentum states and are only constrained by Pauli exclusion principle symmetry. This more exotic pairing mechanism leads to a superconducting gap structure that intersects the Fermi surface at nodes along lines or points (c); consequently, power law temperature dependencies of the physical properties are expected.

A simple picture of how magnetic excitations mediate the Cooper pairing is shown in panel (d). A conduction electron coupled to a localized magnetic moment ( $f_1$ ) through an antiferromagnetic exchange mechanism. If the two localized moments are also antiferromagnetically coupled to each other, then a second conduction electron also influenced by the other localized moment ( $f_2$ ), will then be attracted to the first one.

PLUTONIUM  
SUPER-  
CONDUCTORS



topic underlying many aspects of the nuclear stockpile. (For more information on damage mechanisms in aging plutonium, see the articles by Thomas Zocco and collaborators in *Actinide Research Quarterly* 4<sup>th</sup> Quarter, 2001, and Wilhelm G. Wolfer in *Los Alamos Science* No. 26, 2000.)

**Bridging the gap**

Perhaps the most remarkable result to come from the NMR measurements is the universal scaling of the spin lattice relaxation rate of the unconventional superconductors CeCoIn<sub>5</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (a high-T<sub>c</sub> cuprate material), and PuCoGa<sub>5</sub> in both the superconducting and normal states. This scaling property implies that all three types of superconductors are identical except for the value of the characteristic energy scale of their spin fluctuations. This energy scale  $k_B T_{sf}$  varies linearly with the superconducting transition temperature; the larger the value of  $T_{sf}$ , the higher the T<sub>c</sub>.

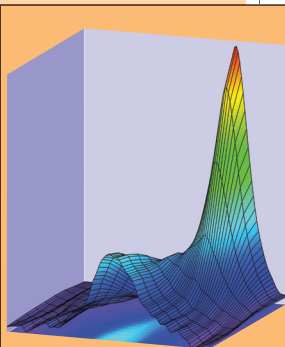
The plutonium-based superconductors with their intermediate transition temperatures bridge the gap between the heavy-fermion superconductors with very low values of both T<sub>c</sub> and spin fluctuation temperature, and the high-T<sub>c</sub> cuprates, which have very high spin fluctuation temperatures and, hence, high transition temperatures. This intimate connection between seemingly disparate classes of materials is quite profound in that it gives hope that other compounds may be found within this universal class of superconductors that have transition temperatures far exceeding the ones currently known.

**Future directions**

While the discovery of superconductivity in PuCoGa<sub>5</sub> was serendipitous—it was also exactly the right place to look. Following the pioneering work of Bernd Matthias in the 1950s and 1960s, we know that certain families of materials “like” to superconduct. Many of the heavy-fermion superconductors, including the first

one ever discovered (CeCu<sub>2</sub>Si<sub>2</sub> by Franck Steglich in 1979), belong to the family of compounds that crystallize in the ThCr<sub>2</sub>Si<sub>2</sub> tetragonal structure. Obviously, the “115” system should also be included on the list of superconducting families.

**Knight shift of PuCoGa<sub>5</sub>**



The nuclear magnetic resonance (NMR) spectra of the gallium in PuCoGa<sub>5</sub> show the dramatic changes that occur below the transition temperature T<sub>c</sub>. The horizontal axis in the front is frequency, the horizontal axis going into the page is temperature, which varies from 20 kelvin (T>T<sub>c</sub>) at the farthest end, and decreases toward 2 K as one moves forward; the vertical axis is intensity. Below T<sub>c</sub>, the intensity drops dramatically because of the decrease in the penetration depth, and the spectral weight shifts to the left (lower frequency) because of the decrease in the magnetic susceptibility in the superconducting state. This shift to lower frequency below T<sub>c</sub> is an indication that the two paired electrons have opposite spin states, known as spin-singlet pairing and thus reveals information about how the electrons bind together.



We also know of another place to look for exotic superconductivity. Nearly all of the known heavy-fermion superconductors are found quite close to a quantum critical point; similar proximity to a quantum critical point in all probability occurs in the copper oxide superconductors as well. A quantum critical point is where a second-order phase transition (usually magnetic in origin) has been suppressed to absolute zero temperature. At this critical point, temperature fluctuations no longer govern the physical properties. Instead, quantum fluctuations now determine the behavior of the system near the critical point; these quantum fluctuations are so strong that their associated peculiarities extend quite far to finite temperatures.

While quantum criticality is well established in many high- $T_c$  cuprates and heavy-fermion

superconductors, there are tantalizing hints that the plutonium superconductors may reside close to a quantum critical point. High-quality single crystals will not only be essential for finding superconductivity in other plutonium-based compounds, but will be an invaluable tool for answering an important question: Are the critical fluctuations that are most violent and abundant near the quantum critical point responsible for the unconventional superconductivity? With the discovery of the  $\text{PuMgGa}_5$  superconductors and a diligent search for other such materials already under way, we are now poised to address this question. In the search for new plutonium intermetallic compounds, the complexity of plutonium may work in our favor—Nature is sure to have some surprises in store.

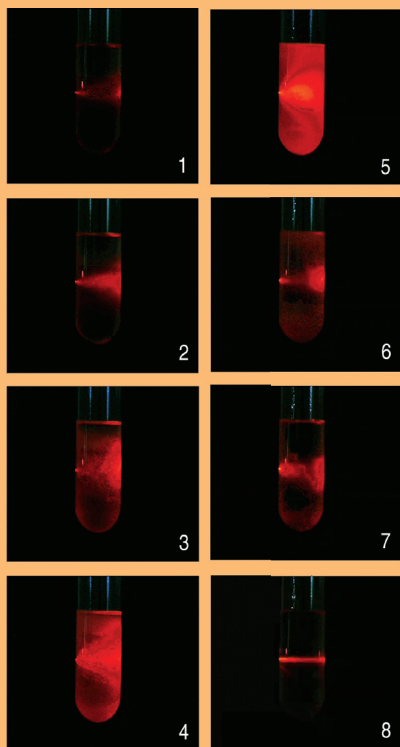


*Polycrystalline samples are often annealed to stabilize one crystallographic phase or to improve crystallinity. In this case, samples of  $\text{CeCoIn}_5$  are quenched in liquid nitrogen after annealing at 600 degrees Celsius. Researcher Eric Bauer removes the sample from the furnace (top) and places it in a vessel containing liquid nitrogen (center). A close-up of the vial in the quenching bath is shown in the lower photo.*

### A different kind of criticality

A mixture of two liquids can exist as two separate phases or as a single phase, depending on the temperature. As two immiscible liquids are heated, the meniscus, which separates the two phases, begins to move (1-3); eventually the two distinct liquids are no longer discernible close to the transition temperature  $T_c$  (4 and 5). The domains in the mixture fluctuate easily between these two phases whose densities are different. These density fluctuations grow in both length and time upon approaching  $T_c$  and reach length scales on the order of microns, a fraction of the wavelength of light. At the transition temperature (or critical point), light is scattered most strongly and the mixture will appear cloudy; this is known as critical opalescence (5). As the mixture is heated further (6-8), the fluctuations decrease rapidly and, therefore, do not scatter light effectively.

An analogous situation occurs at a quantum critical point. In this case, one still goes from a disordered phase (two liquids) to an ordered phase (one liquid), but the fluctuations are no longer associated with density; instead, the fluctuations are quantum mechanical in nature, controlled by the Heisenberg uncertainty principle. Since the critical point is at zero temperature, a control parameter other than temperature is needed to drive the system from the ordered to disordered phase. An example is the suppression of a magnetic phase transition to  $T = 0$  kelvin by the application of pressure. Interestingly, the quantum fluctuations that are strongest near the quantum critical point affect the system even at finite temperatures and, hence, can be observed by experiment. There are indications of this so-called quantum criticality in  $\text{PuCoGa}_5$ , and quantum fluctuations associated with nearby antiferromagnetism may be related to the unconventional superconductivity.



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*The journey ends*

## Fuel assemblies reach their final destination

This article was contributed by David Alberstein of the Nuclear Materials Technology (NMT) Division.

The mixed-oxide (MOX) fuel assemblies fabricated in France from plutonium oxide purified at Los Alamos have been returned to the United States and successfully tested in a commercial nuclear reactor. (See article in *Actinide Research Quarterly* 1st Quarter, 2005.)

Four French FS-65 shipping packages, each containing one lead assembly, and two additional FS-65 shipping packages, each containing fuel rods left over from the lead assembly fabrication campaign, were shipped to the United States by sea from France in mid-April. Los Alamos staff, led by Keith Lacy of Nuclear Materials Management (NMT-4) and Alvin Valdez of HazMat Packaging and Transportation (SUP-5), loaded the packages onto DOE Office of Secure Transport trucks at the Charleston (South Carolina) Naval Weapons Station.

The four packages containing the lead assemblies were delivered to the Catawba Nuclear Station in South Carolina in late April. Tim Stone of NMT-4 and Dave Alberstein of NMT-DO participated in receipt activities at

Catawba. The assemblies were loaded into the Catawba Unit 1 reactor core in late May during a scheduled refueling outage. The reactor has since returned to full-power operation, and the four lead assemblies are producing enough power for about 20,000 households in North Carolina and South Carolina. At the same time, there is a net destruction of about 21 grams of plutonium each day in the four assemblies. The remainder of the plutonium in the MOX fuel is being degraded so that it will no longer be attractive for use in nuclear weapons.

The two FS-65 packages containing excess fuel rods were delivered to Los Alamos for storage in mid-May. The fuel rods will be stored at Los Alamos until startup of the Mixed Oxide Fuel Fabrication Facility at the Savannah River Site (SRS), currently scheduled for 2009, at which time the fuel rods will be shipped to SRS. DOE is considering having Los Alamos disassemble the fuel rods and remove the fuel pellets to reduce the volume of material to be shipped to SRS. A decision regarding this option is expected later this year.

*Two of these FS-65 shipping packages containing excess fuel rods will be stored at Los Alamos until the Mixed Oxide Fuel Fabrication Facility at the Savannah River Site starts up.*



Cogema Inc.



Judging a science fair makes an impact

## About chickens and rocket science

**EDITOR'S NOTE:** Ralph Zehnder held a postdoctoral appointment at Los Alamos for more than two years. His mentors were David Hobart of Chemistry (C) Division and David L. Clark of the Seaborg Institute in the Nuclear Materials Technology (NMT) Division.

Zehnder's early research focused on the dissolution of uranium oxides using peroxide and alkali media in support of the development of the new fuel cycle initiative. More recently he studied the stability of lanthanide inorganic complexes in his research of potential nuclear waste forms.

Because the same synthesis properties most likely apply to both lanthanides and actinides, the lanthanides serve as surrogates, and the procedures developed for the lanthanides are intended to then be applied to the actinide elements. He also has been involved in the synthesis of uranium organometallic compounds as an effort to extend the understanding of fundamental uranium chemistry.

Zehnder received his Ph.D. from the University of Siegen, Germany, and conducted his doctoral research in organometallic chemistry at the University of Idaho, Moscow. This fall he will join the faculty of the University of Louisiana at Monroe as an assistant professor of chemistry.

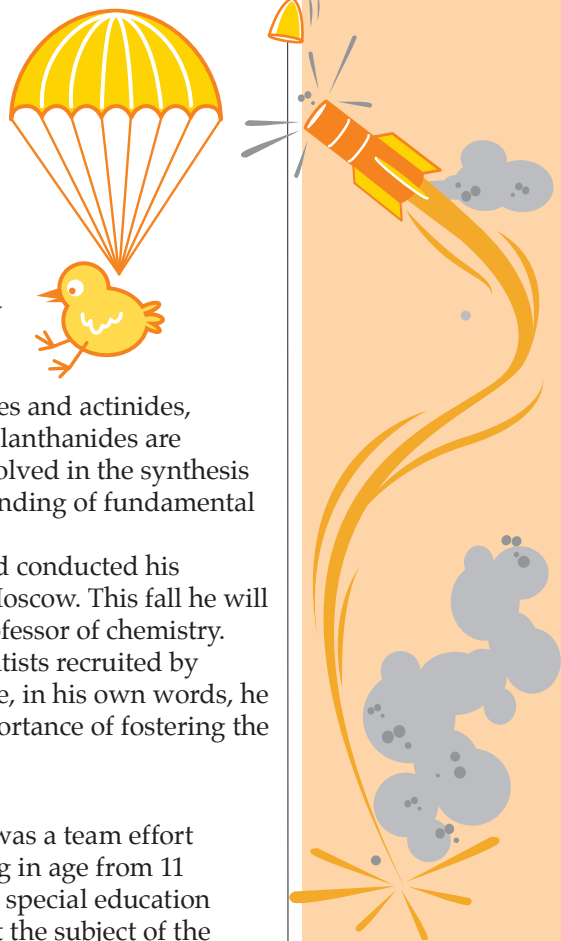
Earlier this spring Zehnder was one of about a dozen Los Alamos scientists recruited by Alan Gurevitch of NMT-12 to judge an elementary school science fair. Here, in his own words, he describes that experience and the impact it has had on his view of the importance of fostering the next generation of scientists.

When Alan Gurevitch asked for volunteers to help judge a science fair at Carlos Gilbert Elementary School, I jumped at the prospect. I am always open to new things, and I thought it would be good training for the position I had just accepted as a chemistry professor. As I drove to Santa Fe on the morning of March 28, I had no idea of the impact the events of that day would have on several people's lives, including my own.

The first project I judged was about the stretching behavior of rubber bands at different temperatures. The second was about the reliability of different packing materials for moving companies. I was looking around for a new task when I ran into a group of students who had three little chickens in a cage. The birds were really cute, and I knew they had to be my next judging assignment. Unfortunately, another judge was already there. He must have noticed that I was very excited about the birds because he stepped away and let me take over.

The chicken project was a team effort of eight students ranging in age from 11 to 13 who were part of a special education class. I had no idea what the subject of the presentation was because so far I had only looked at the little birds, so I asked the students to tell me something about it. I hadn't even finished my sentence when a barrage of information was launched at me simultaneously from the six students present. After a teacher enforced a little discipline, each child proceeded to tell me about his or her individual part of the project.

The students had obtained several fertilized chicken eggs from a nearby farmer and then scientifically simulated and established the conditions for hatching chicks. They placed the eggs in an incubator at the specific temperature of 37 degrees Celsius (99 degrees Fahrenheit) and used a rotator to regularly turn the eggs. After twenty-one days three chicks were successfully hatched under laboratory conditions. The birds (two hens and



Article and photos by  
Ralph Zehnder

Illustrations by  
Chris Brigman

## CHICKENS AND ROCKET SCIENCE



a rooster) were seven months old at the time of the science fair.

I looked at the poster presentation and was amazed at how thoroughly the students had researched how a chicken grows from a single cell to hatching. Every piece of information was displayed so neatly and orderly that readers could learn everything they ever wanted to know about the hatching process. The poster was so professional it would have been suitable for presentation at a technical conference, yet it was created by a group of kids who are sometimes misjudged by people who consider themselves “normal.”

I was reminded of something Mitch Throver, the editor of *Triathlete Magazine*, wrote about physically challenged young athletes: “When I was younger, I would feel pangs of guilt and sorrow when I met or saw someone with a significant physical challenge. However, I quickly learned in life that the only thing different about the physically challenged, is that his or her impediments are on the outside where everyone can see them. The rest of us can hide them from others, and sadly, often from ourselves.”

The final step in the judging process was deciding a fair grade for the students’ terrific work. That wasn’t hard to determine because the project was nearly perfect, so I gave them a 97. (I subtracted 3 points for the little bit of confusion at the beginning of the oral presentation, which, however, resulted only from their excitement and enthusiasm.) The kids and I enjoyed our interaction immensely, and I was impressed by how much I learned (or re-learned from my school days) about the hatching process.

I went on to judge a fourth project about a self-made electrical generator, but all the while I kept thinking about the chickens. After the students had left, I went back several times to check on the birds. I met up with Jason Kirkman, the science fair organizing teacher,

and told him I was impressed by the special ed class and in particular with how hard they worked on their presentation. I was delighted to see the potential in these students to become first-class scientists.

A week later I had a voice mail message from Alan saying something about euphoric and happy kids, the impact that my judging had made, and that he had something for me. When I called him back he said the students had made me a thank you card, which he wanted to give to me in person because he had a story to tell me. When we met a few days later, Alan explained to me that the kids had figured out that I had an accent, but they couldn’t tell what my nationality was. Therefore, they wrote “thank you” in several different languages, which was very scientific and increased the likelihood that they would write it in “my” language (in fact, they had four “hits” in my native language). They also



*The subjects of the chicken project are only a few weeks old in this photo.*

remarked on what a good listener I was. My ability to listen would turn out to be the key element of the story Alan had to tell me.

Alan (who’s girlfriend Andria Liesse is a teacher at Carlos Gilbert and works with the mentors of the chicken project students, Bob Stark and Mary Serrano) explained that some



*The rocket head is attached to the parachute.*

special ed kids have difficulty interacting with others. He said that the chicken project team had been thrilled when they were presented with first-place ribbons. They had never received such recognition

before. Now, here was a scientist from Los Alamos National Laboratory who not only was excited about their project and admired their hard work, but who took the time to listen to them and be educated by them. Alan said that when he saw Mary several days after the science fair she couldn't hold back tears when she told him how proud she was of her students and their work.

I wanted to see the chicken project students again and was lucky enough to be invited back on May 20, this time to watch them launch rockets. The eight students had divided into four pairs with each pair talking about one particular kind of rocket. The first pair, Destiny and Brian, explained their air-pressurized water rocket. The rocket consisted of a plastic bottle filled with water connected to a port hooked up to a pipe system. An electrical air pump, driven by a car battery, pressurized the system. Once the pressure reaches a certain level, the rocket will launch, driven by the pressurized air and water mixture.

The second pair, Drew and Brian, built a Lego™ model of a NASA space shuttle. The inside of the model displayed in

detail the cockpit, the space laboratory, the communications center, the satellite, the engine, and the astronaut performing the outside maintenance. Drew and Brian explained how a team of astronauts works together in a space shuttle, and I was able to fill in some gaps concerning the fuel that drives a shuttle. The kids then taught me something: I had no idea that the fuel tanks hold the volume of four Olympic-sized swimming pools.

Beth and Leandro, the third pair, showed me how to launch air rockets. The principle is similar to the water rockets: an air-pressurized system is used to launch the plastic rockets, which can rise to an altitude of about 400 feet. They explained the system very well and I took the opportunity to help them understand why an air pump becomes hot after extensive use to pressurize the launch base.

The fourth pair of young rocket scientists, Jesus and Aaron, explained how gunpowder-driven rockets work. They explained how the electrically wired ignition sets off the gunpowder, which then launches the rocket. They were very interested in hearing from me about the principle of how gunpowder works as fuel in this particular case. Their commercially available high-end rocket was complete with a camera in the rocket head and parachute. Once the rocket head separates from the rocket body at an altitude of about 500 feet, the camera automatically shoots photos. Because this rocket type is quite costly, they launch it only on special occasions like public demonstrations. On the day I was there



*Final preparations are made to complete the electrical connections.*

*A budding scientist explains the theory behind rocket science.*





CHICKENS  
AND  
ROCKET  
SCIENCE



Countdown to air rocket launch.

they used smaller, less-expensive rockets that did not contain cameras.

After the eight of us had discussed the theories behind the different rocket systems, we went outside for some fun. Immediately a group of younger students gathered to watch. The atmosphere was very much what I would expect at a real NASA launch: a mixture of anxiety and excitement. First off the launch pad were the water rockets, then the air rockets, and finally it was time for the gunpowder-driven rockets. After carefully preparing the electrical wiring for the ignition and taking care to correctly attach the rocket head, the students began the countdown: 10 . . . 9 . . . 8 . . . 7 . . . 6 . . . 5 . . . 4 . . . 3 . . . 2 . . . 1 . . . ignition, and nothing happened. After making some adjustments to the electric wiring, the students began a second countdown: 10 . . . 9 . . . 8 . . . 7 . . . 6 . . . 5 . . . 4 . . . 3 . . . 2 . . . 1 . . . ignition, blastoff!

At the end of the day I thought about the remarkably synergistic way in which the kids and I had educated each other; each one of us learning scientific facts we had not known before. This shows that teaching is not one-way but a back-and-forth flow of information, and that at times it is hard to distinguish teacher from student. (This reconciles with Heisenberg's principle of uncertainty, distorting the actual role of teacher and



Postdoc Ralph Zehnder (at left), teachers Bob Stark (kneeling at right) and Mary Serrano (standing at far right), and some of the chicken project-rocket science students pose for a photo after the successful rocket launches.



The technical area used for rocket tests.

student.) And as I drove home, I realized that my experience with the students and their teachers had profoundly affected me.

In my opinion, Bob Stark and Mary Serrano are everyday heroes. They have been with these kids for the last seven years and have prevented them from falling through the cracks. This particular class will enter junior high next school year, and I worry about what will become of them without the nurturing of Bob and Mary. I hope they find equally caring teachers who see them for the amazingly bright group of kids they are and who encourage their attempts at scientific experimentation.

My experiences with the chicken project team have inspired me, and I would like to become a driving force in community outreach when I settle into my new life as a professor at the University of Louisiana. It is essential for us to recognize and reward the hard work of teachers, support them in their difficult job, and aid our community and schools through outreach activities like judging science fairs. It also is essential that we step up today to mentor students of all ages, from preschooler to postdoc, because they will be the driving force in determining tomorrow's science. I've learned that being a hero doesn't take superhero strength: all it takes is time—and the ability to listen.

*P.S. The chickens are alive and well and being cared for by a Carlos Gilbert teacher.*



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