


Los Alamos National Laboratory  
**ACTINIDE RESEARCH  
QUARTERLY**

3rd/4th quarter 2005

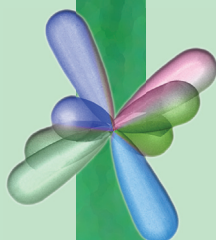
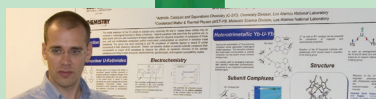
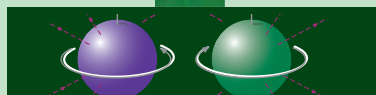
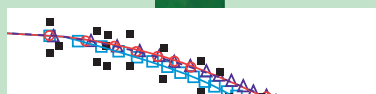


**Correlation effects  
in actinide systems**

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ACTINIDE RESEARCH QUARTERLY

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*New theories needed to describe actinide elements*

## Correlated electron effects for anomalous properties of elemental actinides

**EDITOR'S NOTE:** A group of international experts in materials and many-body physics met at Los Alamos in May 2005 to discuss the issues of electron correlations in materials and in the actinides or actinide systems in particular. The workshop was sponsored by Los Alamos' Materials Science and Engineering Council, the Seaborg Institute, and Taylor & Francis Informa PLC. This article, as well as the articles beginning on pages 5 and 11 of this issue, discusses research presented at the workshop.

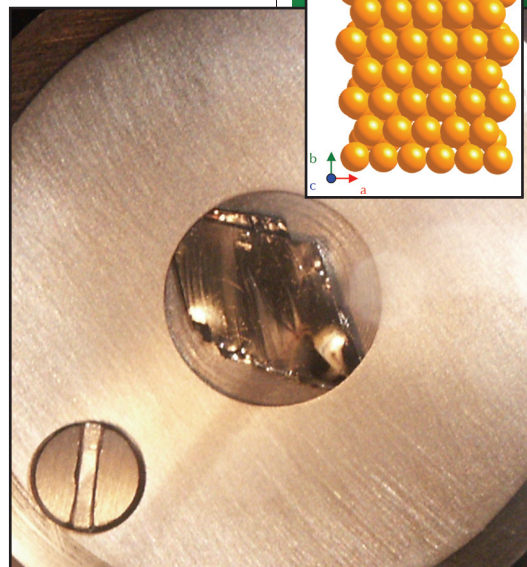
The behavior of many materials, including macroscopic phenomena such as magnetism, conductivity, and perhaps more-global physical properties such as strength and chemical reactivity, are generally governed by the electronic properties of the material. For many systems, these properties can be qualitatively explained and predicted by assuming that any given valence electron in the material is independent (aside from the exclusion principle) from the others and behaves without concomitant knowledge of the positive ion background from the nuclear cores of the crystal lattice. These materials behave in a common universal manner and were called Fermi liquids by Lev Landau.

There is overwhelming evidence, however, that this simple situation is not the case in the transuranic elements, including uranium and plutonium. In fact we speculate that the unusual physical behavior of the actinides, which includes numerous distinct thermal allotropes for a specific element, and unusual electronic behavior, are very likely the effect of strong electron–electron correlations and/or significant electron interaction with crystal lattice vibrations (phonons) or other quasiparticles in the system, such as paramagnons and polarons.

The availability of very high-quality single-crystal specimens is crucial for observing the true nature of a material because impurities in many cases dramatically modify the physical properties. (See the article by Harold

McFarlane and co-authors in *Journal of Metals* 49, 1997.) Recently, high-purity single-crystal platelets of alpha ( $\alpha$ )-uranium have been available. These single crystals appear to have very high purity and low defects, making them ideal for studies of fundamental behavior. The first measurement that indicated new unusual behavior in uranium reported a softening (decrease) in the phonon density of states in  $\alpha$ -uranium as it was heated from 50 to 950 kelvin (K), where it was shown that the interatomic potential remains harmonic, and thus these changes are not explained by simple thermal expansion. The measurement indicated that there was a large, unexplained

*This alpha ( $\alpha$ )-uranium platelet single crystal shows an atomically clean uranium (001) surface in ultrahigh vacuum after cleaning and annealing to restore surface order. Note that the overall shape of the crystal reflects the symmetry of atomic order in the material. The uranium single crystal is mounted on a molybdenum sample carrier for good thermal contact and captured lightly at the corners to avoid strain effects during annealing to 600 degrees Celsius.*

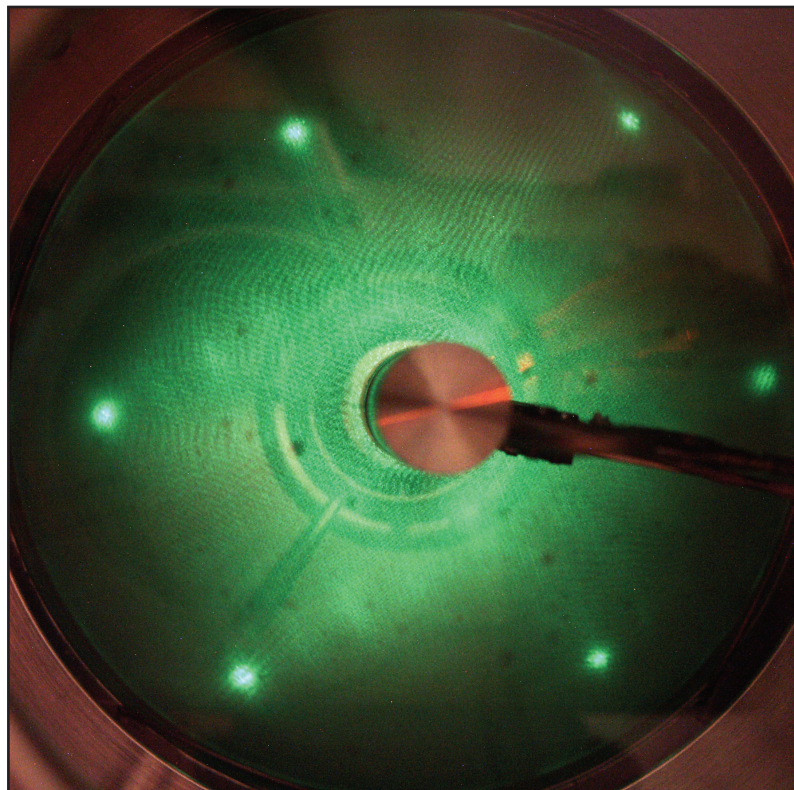


This article was contributed by Roland Schulze and James L. Smith of the Materials Science and Technology Division and Krastan Blagoev of the Theoretical Division.

*The inset shows a real-space representation of the atomic arrangements of the alpha ( $\alpha$ )-uranium (001) surface. The orthorhombic structure of  $\alpha$ -uranium leads to a stretched hexagonal arrangement of atoms at this surface. Note that this surface can also be viewed as chains of uranium atoms running along the (010) direction.*

## CORRELATED ELECTRON EFFECTS

This is a low-energy electron diffraction (LEED) measurement of the atomically clean and ordered alpha ( $\alpha$ )-uranium (001) surface. The bright spots in the image are a measurement of the long-range atomic order of the surface of the uranium single crystal. The measurement here is in effect a reciprocal space representation of the true atomic surface order of the illustration of the uranium (001) atomic surface on Page 1. The measurement indicates a relatively well-ordered surface with no indication of surface reconstruction.



increase in entropy at higher temperatures. (See the article by Michael Manley and co-authors in *Physical Review Letters* 86, 2001.)

The initial suggestion was that an exchange coupling with electronic energy or entropy led to this behavior, and indeed, photoemission measurements of the electronic density of states at the Fermi level indicated an anomalous broadening (an unexpected increase in the system electronic energy) with temperature. This may be linked directly to the increase in entropy in the phonon density of states.

Furthermore, it has now been observed that small amounts of impurity elements in solution in  $\alpha$ -uranium have a similar but opposite effect in the phonon behavior. These observations clearly need to be understood at a basic level.

These and other observations over many years have led to increasing interest in the

possibility that electron correlation effects govern the behavior and physics of many materials and in particular those of the actinide series. As has been discussed frequently (in previous issues of *Actinide Research Quarterly* and the "Challenges in Plutonium Science" issue of *Los Alamos Science*, 2000), one can observe the very unusual behavior revealed in plutonium, where the metal exhibits five solid phases. These five phases have widely varying crystallographic structures as a function of temperature and impurities, negative thermal expansion coefficients for some phases, and a contraction to higher density upon melting.

Uranium, likewise but to a lesser extent, also shows some of this unusual behavior.

The unique behavior in plutonium arises from the interaction of the 5f electrons. For the early actinides these f-electrons are itinerant (delocalized), while for the actinides past plutonium the f-electrons appear to be localized and therefore more core-like and noninteracting. The point of transition in plutonium occurs when a small input of energy in the form of thermal promotion or perhaps a change in entropy causes an itinerant-to-localized crossover as the plutonium moves through the low-temperature to high-temperature allotropic phases.

We believe that the equally unusual behavior observed in uranium as a function of temperature, showing only three allotropic solid phases before melting, coupled with the

new phonon and electron measurements, is a consequence of the same physics exhibited in plutonium, but short of the drastic transition of the f-electron system from itinerant to localized behavior. As such, the availability of high-quality uranium single crystals is a great boon, allowing unprecedented control in the experimental measurements not previously possible. This has caused a renaissance in recent investigations of this system and should prove to be of great benefit in leading to a deeper understanding of the unusual behavior in the actinides in general, as well as in systems where correlation effects are expected to play dominant roles in their physics.

The recent work described above, as well as the work of Los Alamos researchers Robert Albers, Dan Thoma, Cyril Opeil, and Jason Lashley, had suggested that new theories to describe the actinide elements, both pure and impure, were needed. The May workshop was intended to inform the community interested in this problem of recent results and to solicit expert opinion on future experimental and theoretical needs to further the knowledge of these unusual elements.

The workshop included presentations from the following invited external experts: Kevin Bedell, Boston College; George Chapline, Lawrence Livermore National Laboratory; Zachary Fisk, University of California, Davis; Miklós Gulácsi, Australian National University, Canberra; Gabriel Kotliar, Rutgers; Peter B. Littlewood, director, Cavendish Laboratory, Cambridge, England; David Pines, Institute for Complex Adaptive Matter; and Peter S. Riseborough, Temple University.

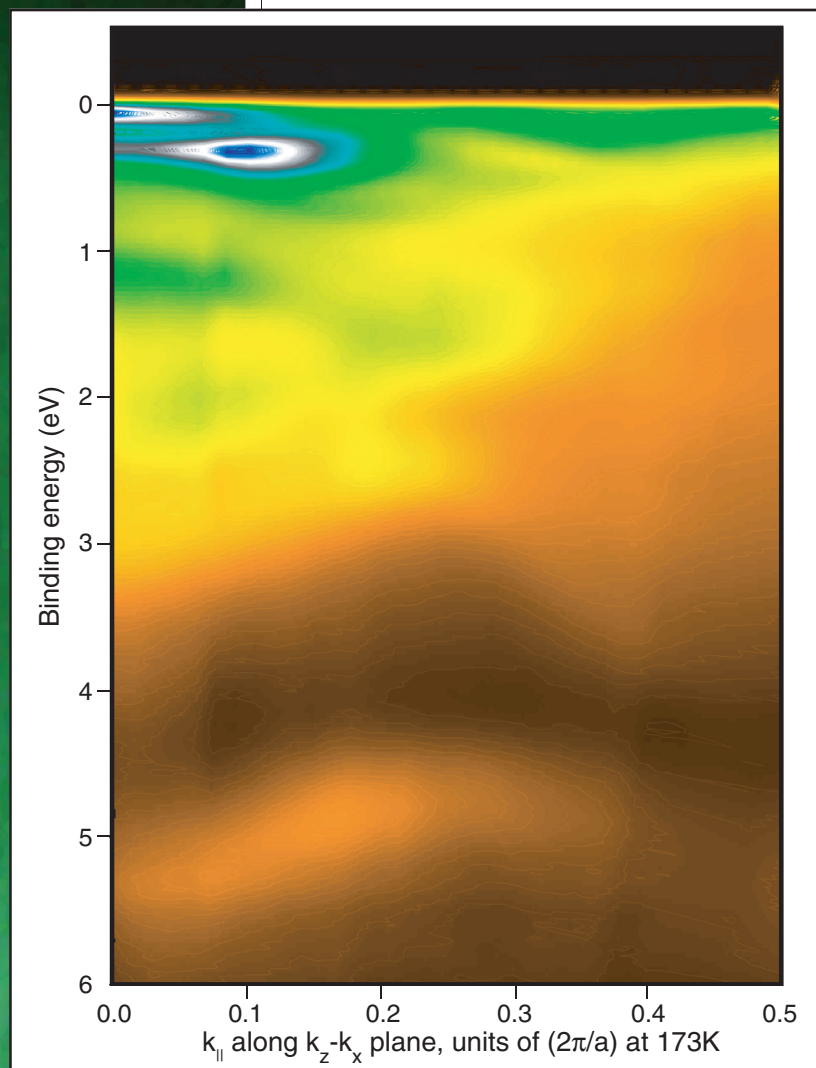
Los Alamos scientists pursuing research in these systems also made presentations. They included Manley, James L. Smith, Opeil, Bogdan Mihaila, Nicholas Curro, Lashley, Krastan Blagoev, Richard Martin, Roland Schulze, John Singleton, and Albert Migliori. David Clark presented a broad perspective

on actinide behavior ranging from actinide molecular chemistry to condensed-matter physics and the connection between the two. Smith provided a historical perspective of actinide condensed-matter physics and an introduction to the new measurements. Manley, Opeil, Curro, Lashley, Migliori, Singleton, and Schulze described these measurements in detail.

Workshop participants discussed the new approaches that have been developed in the past few years to treat these systems in light of the new experimental measurements. These discussions included presentations by Pines on emergent behavior in f-electron systems, Gulácsi on mean field theoretical approaches to explain the new phonon measurements, Kotliar on the use of dynamical mean field theory (DMFT) approaches to model electronic correlations in the actinides, Mihaila on the possibility of future experiments yielding a measurement of the Eliashberg function to derive directly the electron-phonon coupling behavior, and Littlewood on generalized theoretical approaches to these systems. Bedell and Blagoev presented new theoretical approaches to understanding superconductivity in the  $UGe_2$  system.

Additional presentations included Fisk's discussion of the importance of treating coherence in these types of systems, while Martin discussed new successful theoretical treatments of molecular or molecular-like actinide systems by hybrid density functional theory. Riseborough discussed new theoretical treatments of  $\alpha$  and gamma ( $\gamma$ ) cerium, while Chapline spoke on plutonium and quantum critical points.

The workshop ended with a roundtable discussion that solicited new ideas and directions in experimental measurements and theoretical treatments required to address correlation effects in these actinide systems. As had been highlighted by the results on the new

CORRELATED  
ELECTRON  
EFFECTS

*This plot is the first electronic bandmap measurement of the alpha ( $\alpha$ )-uranium (001) surface. It represents a small portion of the electronic structure of uranium in crystal-momentum space. The electronic bands in uranium (the bright areas) are shown as a function of electron binding energy and electron momentum within the crystal. There are sharp bands near the Fermi edge at  $<0.1$  and  $0.3$  electronvolt (eV). In addition there are bands at  $1.1$ ,  $2.1$ ,  $3$ , and  $5.5$  eV that disperse as a function of crystal momentum,  $k_{||}$ .*

uranium single crystals, the area of materials synthesis and control toward cleaner, more-ordered materials was elevated as a priority to pursue. This included growth of pure materials and especially single crystals, as well as the possibility of using compounds designed to effectively “clean” the actinide.

The second area of priority was discussion of crucial experiments needed on available, or soon-to-be produced, high-quality materials. These included a variety of standard techniques to measure physical properties, but suggested an expanded use of real-space probes such as transmission electron microscopy and scanning tunneling microscopy to image atomic ordering or disordering. The third area of priority was development of new theoretical treatments, which would lead to the inclusion of correlation effects in a material-specific model of these materials. This was discussed as a critical area, which is now ripe for expansion in the vein of Kotliar’s DMFT approach to modeling these systems. This is especially important because the fine details of the electronic properties are emerging in the experimental studies.

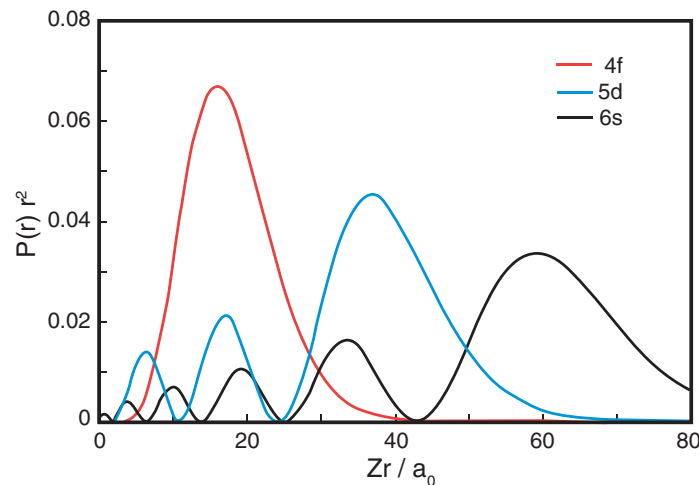
The workshop provided two days of presentations of progressive work and ideas as well as stimulating discussion in actinide condensed-matter research. It was agreed by many of the participants that new methods and paradigms are needed to understand the recent experimental results, with the possibility of correlation effects playing a strong role in the observed physics. The group hopes to meet on a regular basis.

*An exception to the trend*

## The gamma-to-alpha transition in cerium

The phase diagrams of solids frequently exhibit structural transitions in which the symmetry of the structure is lowered as the temperature is lowered. The gamma-to-alpha ( $\gamma \rightarrow \alpha$ ) transition in cerium, first discovered by Andrew Werner Lawson and Ting-Yuan Tang in 1947, provides a notable exception to this trend because the atoms retain their ordering in a face-centered cubic structure while the volume changes by almost 17 percent. Moreover, the high-temperature  $\gamma$  phase has a large and temperature-dependent Curie-Weiss susceptibility, whereas the low-temperature  $\alpha$  phase has a small and almost temperature-independent susceptibility.

Because cerium is the first element in the lanthanide series, it could be expected that the anomalous change in the volume may be related to the anomalous lattice vibrations of uranium. However, a major difference between cerium and uranium occurs because the electrons in the 4f shell of atomic cerium are shielded by the outer 5d and 6s electrons. Soon after Lawson and Tang's discovery, Linus Pauling and William H. Zachariasen independently interpreted the transition in terms of the promotional model, in which all the electrons are being squeezed out of the innermost 4f shell into the 5d-6s conduction band to participate in the bonding.



Karl Gschneidener, Jr. and co-workers at Ames Laboratory later modified the promotional model by proposing that not all the electrons were squeezed out of the 4f shell. In the late 1960s, however, Dan Gustafson and co-workers at Wayne State University performed

This article was contributed by Sukalpa Basu and Peter S. Riseborough of the Department of Physics, Temple University.

*This schematic shows the radial variation of the probability density  $P(r)$  for finding an electron at a radial distance  $r$  from the nucleus for the atomic 4f, 5d, and 6s states.*

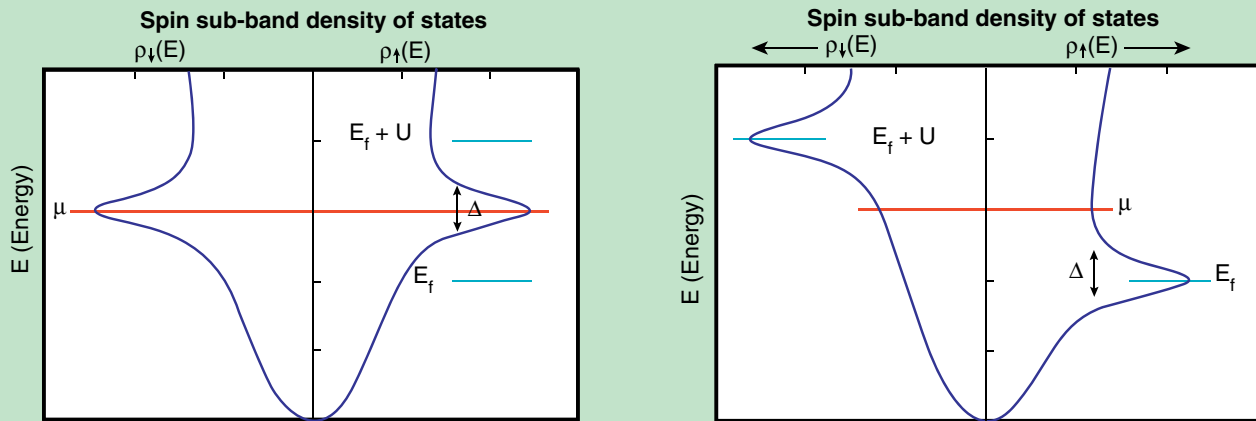
GAMMA-TO-ALPHA TRANSITION

positron annihilation experiments on cerium and found that the change in the number of conduction electrons was inconsistent with the change invoked in the promotional model.

In 1977, Börje Johansson, then at Uppsala University, suggested that the transition was an example of a Mott transition, which is due to the competition between the coulomb interaction energy between pairs of electrons on an atom. A Mott transition can be written in terms of the number of electrons with spin up  $\eta\uparrow$  and spin down  $\eta\downarrow$  as

$$H_{int} = U\eta\uparrow\eta\downarrow .$$

When  $U$  is greater than the bandwidth  $\Delta$  (which represents the kinetic energy of 4f electrons that move between the atoms), electrons are prevented from hopping onto a 4f orbital that is already occupied by an electron. The Fermi energy  $\mu$  is defined as the energy of the highest occupied state. In this localized state, the spin-up and spin-down density of states are split so that the peak in the spin-up density of states lies below the Fermi energy and is occupied, while the peak in the spin-down density of states is located above the Fermi energy and is mostly unoccupied. Hence, there is a net localized magnetic moment.



The total density of states shows a sharp peak from the 4f density of states and a broad component from the conduction band. The spectra of the nonmagnetic state are shown on the left, and the spin-split spectra of the local moment state are shown on the right.

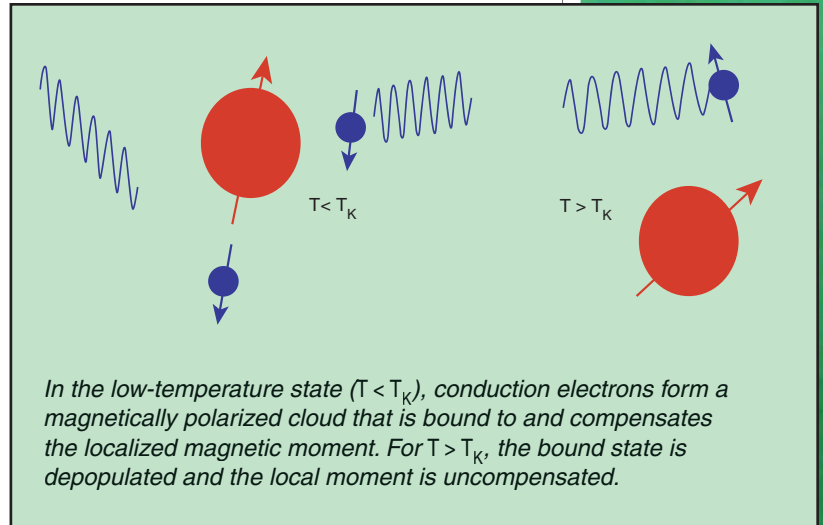
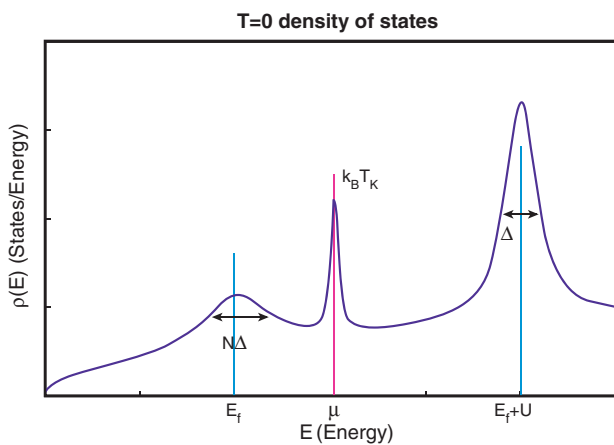
On the other side of the transition where  $U$  is less than  $\Delta$ , the electrons travel between all the 4f shells of all the atoms. This state is nonmagnetic because both peaks in the 4f density of states at  $E_f$  are pinned at the Fermi energy. Consequently, there should be a concomitant change in the electron excitation spectra at the Mott transition. The excitation spectrum of cerium from photoemission experiments was found to be inconsistent with Johansson's picture. However, recent calculations indicate that besides the peaks in the spectra above and below the Fermi energy, the spectra may contain a narrow peak near the Fermi energy similar to the spectrum of the model developed by the Nobel Prize winner Philip W. Anderson to describe the Kondo effect.



In 1982, Jim Allen and Richard Martin developed the Kondo volume collapse model (consistent with the photoemission data) where the residual interaction between the localized magnetic moments in the 4f shell with the spins of the conduction electrons results in conduction electrons being bound to the local moments such that the net moment cancels. For temperatures below a characteristic temperature  $T_K$  known as the Kondo temperature, the bound states are occupied and the system is nonmagnetic. For temperatures greater than  $T_K$  the electrons are thermally excited so that the bound states are unoccupied and the localized magnetic moment is uncompensated. Furthermore, in this model  $T_K$  is volume dependent and changes from the small value of 70 kelvin (K) in the  $\gamma$  phase to 812 K in the  $\alpha$  phase.

Inelastic neutron scattering experiments performed in 1983 at the Institut Laue-Langevin in Grenoble, France, by Amir Murani and co-workers have shown that the energy needed to excite the nonmagnetic local moments in the  $\alpha$  phase is about 150 meV ( $T_K \sim 1740$  K), which is two times larger than the value of 812 K initially suggested. Other measurements performed at Los Alamos in 2001 by Robert McQueeney and co-workers on the high-temperature  $\gamma$  phase showed a quasi-elastic peak consistent with the assumed small Kondo temperature along with a small and very broad feature, which indicates that the cubic crystalline environment of the atomic 4f magnetic moments produces an orientational anisotropy in the energy of the moments.

Recently, several groups at Los Alamos have investigated the effects of the thermal disorder that appears as vibrations of the atoms in the solid, using inelastic neutron scattering and X-ray diffraction. As predicted by Peter J.W. Debye and later by Ivar Waller, the thermal vibrations of the atoms reduce the intensity of the peaks of the elastically scattered X-rays. From the measured



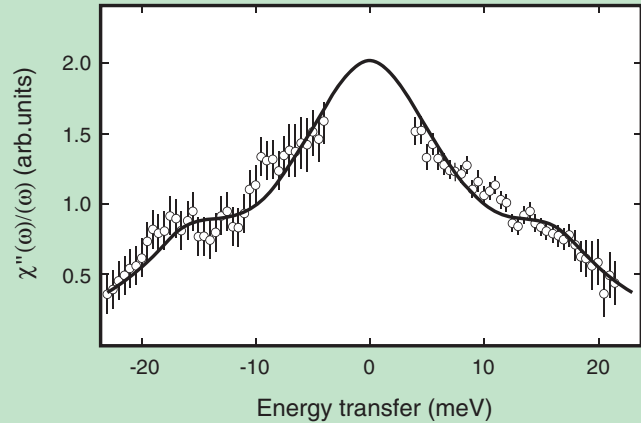
intensities of the X-ray peaks, Il-Kyoung Jeong and co-workers at Los Alamos inferred that there was a significant discrepancy between the change in thermal disorder at the transition and the amount of change needed in the Kondo volume collapse scenario.

In 2001, Maxim Dzero, Lev Gor'kov, and Anatolii Zvezdin from the National High Magnetic Field Laboratory in Tallahassee, Fla., suggested that if the transition is due to the competition between thermal disorder of the localized

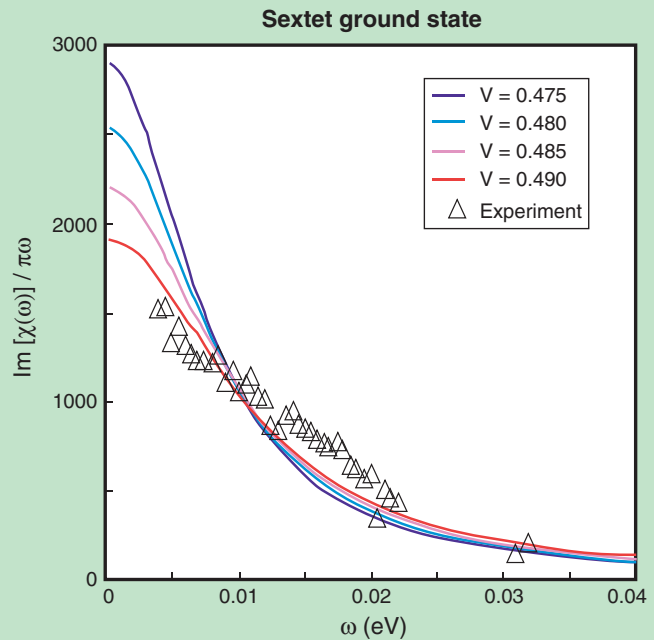
*This schematic shows how the electronic excitation spectrum for Anderson's impurity model describes local moments in metals.*

GAMMA-TO-ALPHA  
TRANSITION

The results of inelastic neutron scattering experiments of Murani and co-authors on the alpha ( $\alpha$ ) phase of cerium. The peak in  $\chi''(\omega)/(\omega)$  occurs at the energy  $\hbar\omega = k_B T_K$  required to excite the electrons out of the Kondo bound state, thereby creating the uncompensated 4f local moment.



The results of inelastic neutron scattering experiments of McQueeney and co-workers on the gamma ( $\gamma$ ) phase of cerium. We have superimposed our calculated spectra for the single-impurity Anderson model for various values of  $T_K$  and no crystal field splitting. The observed inelastic scattering data are consistently above the theoretical values near 17 meV, which is indicative of a cubic crystal field splitting.

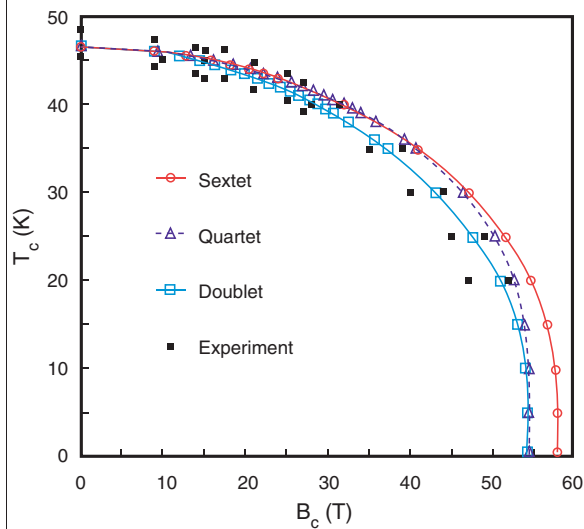
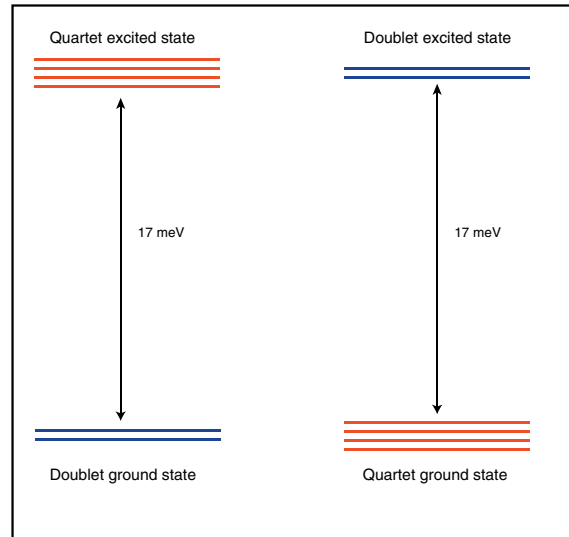


magnetic moments and field-independent condensation energy, then an applied magnetic field should result in a change in the phase diagram. In particular, they predicted that the phase boundary in the ( $B, T$ ) plane should have the form of a quarter of an ellipse as was confirmed at Los Alamos in 2005 by Fivos Drymiotis and co-workers. They doped cerium with thorium and lanthanum to depress the zero-field transition temperature to such an extent that it would be possible to measure the entire phase boundary with the magnetic fields currently available.

Because the inelastic neutron scattering experiments of McQueeney and co-workers on  $\gamma$  cerium had indicated that the cubic crystalline electric field lifts the degeneracy of the spin states by moving some of them to higher energies, we expected that the crystal field splitting should reduce the amount of thermal disorder above the phase transition and also affect the energy lowering due to the magnetic field. We have incorporated the cubic crystal field into the single-impurity Anderson model to describe the inelastic neutron scattering results of McQueeney and co-authors.

On applying the resulting theoretical picture to the experimentally determined  $(B, T)$  phase boundary of  $\text{CeLa}_{0.1}\text{Th}_{0.1}$  we found that there was a slight deviation of the theoretical prediction of Dzero and co-authors from the experimental curve, which is completely consistent with the existence of the cubic crystalline electric field and a doubly degenerate ground state. The crystalline electric field does affect the free-energy balance of the first-order phase transition, and its identification allows for a more accurate determination of the effects that the lattice and its thermal vibrations have on the volume anomaly.

The work at Temple University was funded by the U.S. Department of Energy, Office of Basic Energy Sciences.



*The possible crystal field splittings of the  $4f^1$  state of cerium in a crystal with cubic symmetry.*

*The  $(B, T)$  phase diagram of  $\text{CeLa}_{0.1}\text{Th}_{0.1}$ . The error bars of the experimental data of Drymiotis and co-authors are shown by the black squares and the predictions of Dzero and co-authors, which do not include the splitting due to the crystalline electric field, are shown in red. Our results, which include the experimentally observed crystalline electric field and assume either a 2-fold degenerate ground state or a 4-fold degenerate ground state, are shown by the blue lines.*



Photo by Mick Greenbank



ADVANCING SCIENCE, SERVING SOCIETY

## ARQ scientific advisor named

### AAAS Fellow

**David L. Clark**, one of *Actinide Research Quarterly's* scientific advisors, has been named a 2005 Fellow of the American Association for the Advancement of Science (AAAS). Clark received the honor for distinguished contributions to the field of actinide science. He is director of the Seaborg Institute for Transactinium Science in the Nuclear Materials Technology Division Office (NMT-DO).

"It is a pleasure to compliment Dave on his being named a Fellow of AAAS and to have him as one of the scientific advisors of *ARQ*," said NMT Division Leader Steve Yarbro. "Dave has supported *ARQ* with his time and his extensive technical knowledge. This association ensures that the technical content of the publication is of the highest quality and is focused on the issues important to the nuclear complex. My congratulations go to Dave on his latest achievement and for his contributions not only to *ARQ*, but to NMT Division and to the DOE complex."

Clark was one of six Los Alamos researchers who received the honor this year. The other five are Richard Keller of Cell Biology, Structural Biology and Flow Cytometry (B-2); Antonio Redondo of Theoretical Biology and Biophysics (T-10); Robert Ecke of the Center for Nonlinear Studies (T-CNLS); Sigfried Hecker, director emeritus of Los Alamos and currently a visiting professor at Stanford University; and Sallie Keller-McNulty, formerly of Decision Applications (D) Division and now at Rice University. A total of 376 members of AAAS were elected Fellows in 2005. They will be recognized at the Fellows Forum scheduled for Feb. 18, 2006, during the annual AAAS meeting in St. Louis.

A Fellow is defined as "a Member whose efforts on behalf of the advancement of science or its applications are scientifically or socially distinguished." AAAS members can be nominated for the rank of Fellow by the steering groups of the association's 24 sections; the chief executive officer; or any three Fellows who are current AAAS members, two of whom are not affiliated with the nominee's institution. Each steering group reviews the nominations within its respective section and presents a list to the AAAS Council, which then votes on the final list.

AAAS, founded in 1848, is the world's largest general scientific society and is publisher of the peer-reviewed journal, *Science*.

## Finding a solution to the puzzles

# Plutonium and quantum criticality

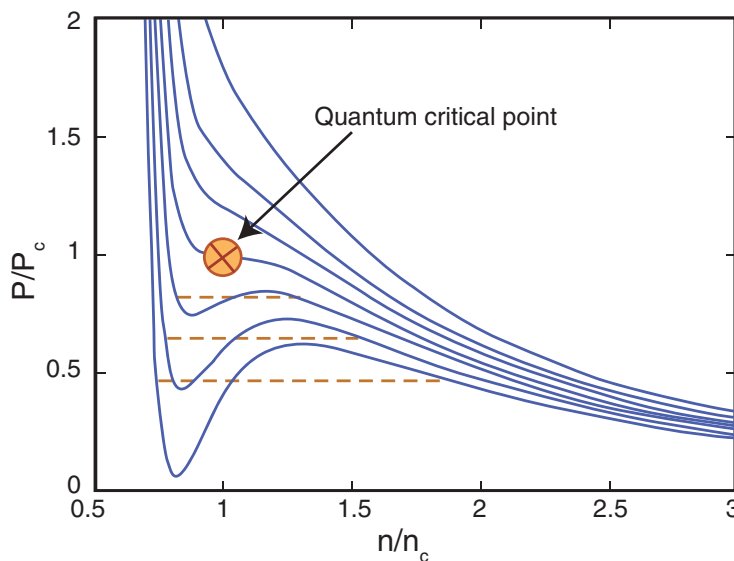
From its onset the Manhattan Project was bedeviled with a peculiar problem: the lattice structure and density of elemental plutonium seemed to have two different values, depending on how it was prepared. Perhaps even more remarkably, despite the importance of this problem and the passing of more than sixty years, we still don't understand why plutonium occurs in these two allotropic forms.

Another mystery is why plutonium is not magnetic. By the usual atomic rules, the valence f-electrons of plutonium should have a non-vanishing angular momentum and associated magnetic moment. However, there is considerable evidence that there are no local magnetic moments in elemental plutonium. More than thirty years ago Bill Nellis showed that at very low concentrations, plutonium impurities in platinum exhibited the expected magnetic moment. However, Nellis discovered that as the concentration increases the magnetic moment rapidly decreases, and quite surprisingly becomes vanishingly small for plutonium concentrations above a few percent.

Fortunately, a solution to these puzzles may be on the horizon. A hint that elemental plutonium lies close to a quantum critical point (QCP) of some kind is that, as a function of relatively modest changes in temperature and pressure, there are a variety of phase transitions that involve changes in both the lattice structure and the electronic state of the 5f electrons. (See the introduction by Jim Smith and me to "Challenges in Plutonium Science," *Los Alamos Science*, 2000.)

The negative thermal expansion of  $\delta$  plutonium is also indicative of critical behavior. Recent studies of radioactivity-induced damage in plutonium carried out at Lawrence Livermore National Laboratory by Mike Fluss and Scott McCall have yielded evidence that these strange phenomena may all be the result of a QCP associated with the existence of a quantum-order parameter in plutonium coupled to lattice distortions. Our guess is that elemental plutonium is a gossamer superconductor, i.e., there is a condensate ground state with off-diagonal long-range order but no bulk superconductivity. More specifically, we believe that in the actinides there is a non-vanishing density of paired itinerant charge carriers and that plutonium lies close to a critical point for this order parameter.

In general, if one plots the pressure of a quantum fluid versus condensate density one will obtain a van der Waals-like curve. For some particular values of the parameters in the Hamiltonian this curve can have a critical point, and I believe that the  $\delta$  form of plutonium can be identified with such a point.



This article was contributed by George Chapline of the Physics and Advanced Technology Directorate, Lawrence Livermore National Laboratory.

The author thanks Jim Smith, Mike Fluss, Scott McCall, Kevin Moore, Christos Panagopoulos, David Santiago, Montu Saxena, Gil Lonzarich, and Jan Zaanen for helpful conversations.

Pressure versus density for a quantum condensate.

PLUTONIUM  
AND QUANTUM  
CRITICALITY

*The lack of inversion symmetry in monoclinic plutonium allows a spin Hall effect in which the electric field from charge carriers creates localized spin currents that carry positive or negative spin polarization, depending on the direction of the spin current. The charge carriers become magnetic monopole-like objects that are naturally paired because the effective magnetic charge is opposite for carriers with opposite spin, causing an attractive interaction for these carriers.*

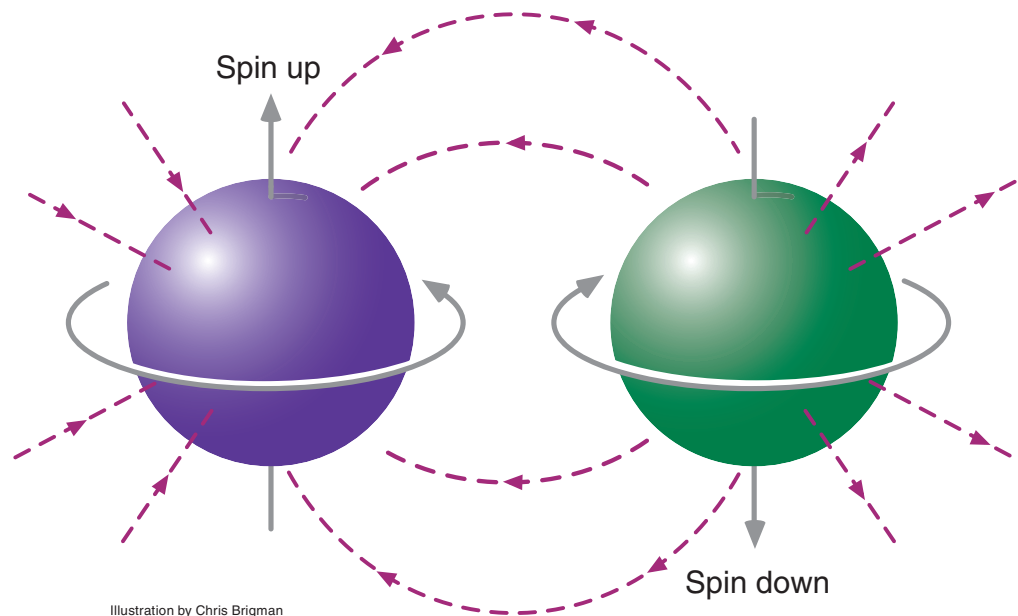
The idea of a gossamer condensate was originally introduced by Bob Laughlin to explain the relationship between superconductivity and antiferromagnetism in high-critical-temperature (high- $T_c$ ) superconductors. Subsequently, it was suggested by Laughlin's students Zario Navario and David Santiago and me in a paper that appeared in *Philosophical Magazine B* in 2005 (Volume 85, Page 867) that there may be a gossamer condensate in all materials that have "metal-bad metal" transitions similar to the  $\alpha \rightarrow \gamma$  transition in cerium. The quasi-particle gap for this condensate would be very small, leading to metal-like behavior for all pressures.

In cases such as elemental cerium, praseodymium, and gadolinium, where the metal-bad metal transition is accompanied by "volume collapse," a plot of the gossamer order parameter versus pressure would correspond to the van der Waals-like "loops" in the figure below, where the transition pressure would be determined by a Maxwell construction (the dotted lines). In other cases, such as elemental neodymium or samarium, or cerium-thorium

alloys doped with lanthanum, where the metal-bad metal transition is continuous, the transition would correspond to the critical inflection point in the figure.

The decrease in electrical conductivity in a gossamer metal is due to a decrease in the number of charge carriers rather than a decrease in carrier mobility. This is a very different picture from that of a Mott metal-insulator transition. In any case, though, the continuous "metal-bad metal" transitions in rare-earth materials cannot be Mott metal-insulator transitions since Mott transitions are always first-order transitions.

That the differences between the alpha ( $\alpha$ ) and  $\delta$  forms of plutonium might be related to the  $\alpha \rightarrow \gamma$  transition in cerium has been discussed for some time. Barry Cooper also pointed out in his article in the "Challenges in Plutonium Science" issue of *Los Alamos Science* that  $\delta$  plutonium may be analogous to the critical point in the phase diagram of uranium sulfide doped with lanthanum where magnetism disappears. Doping with lanthanum changes the 5f-p/d hybridization, and at a critical dop-



ing the 5f electrons become magnetic. As was suggested by Miklós Gulácsi in his talk at this workshop, 5f-p/d hybridization may strongly affect the electron-phonon coupling strength in actinide materials. Mike Manley has suggested checking this by looking at phonon dispersion as a function of lanthanum doping in the case of  $U_xLa_{1-x}S$ .

The possibility that electron-phonon coupling plays an important role in stabilizing the various forms of plutonium is intriguing from the point of view that electron-phonon coupling seems to play a similar role in certain oxide materials. For example, as Neal Mather and Peter Littlewood point out in their article on manganites in the January 2003 issue of *Physics Today*, in  $LaMnO_3$  with approximately 50 percent of the lanthanum ions replaced with an alkaline earth, it is the electron-phonon coupling strength that distinguishes the coexisting metallic and insulating phases.

In these materials there are three localized three-dimensional electrons attached to every manganese ion. In addition, there is an extra valence electron ranging from one per manganese ion at zero doping to none for complete substitution. The strong electron-phonon coupling arises from Jahn-Teller distortion of the oxygen octahedra when the extra valence electrons are localized by the formation of "Zener polarons," where pairs of  $Mn^{3+}$  ions share an electron hole in a bridging oxygen ( $O^-$ ) ion. Amazingly reminiscent of the situation in plutonium, the competition between localization and itinerancy when the number of extra valence electrons is near 0.5 per manganese ion results in a proliferation of phases that can actually coexist in the presence of defects or impurities.

In the case of  $\delta$  plutonium, the last valence electron also hovers between localization and itinerancy. If electron-phonon coupling does indeed depend on f-p/d hybridization, then it certainly seems possible that there

could be a multitude of phases with different lattice structures and degrees of localization of the extra valence electron. However, the mechanism of localization for the extra valence electron in plutonium must necessarily be different from that in the manganites because there are no oxygen ions available to form Zener polarons. Furthermore, none of the phases of plutonium are insulating.

The tendency toward localization of the last valence electron in plutonium may actually be the result of spin-orbit interactions, which are known from X-ray spectroscopy studies to be of considerable importance for the core 5f electrons in the actinides. Even in lower Z materials, spin-orbit effects can be important, e.g., in determining the easy axis of magnetization in ferrites.

Spin-orbit interactions can also lead to an interesting coupling between itinerant spin currents and localized electrical charge if the lattice structure allows an internal electric field. The  $\delta$  form of plutonium would not seem to be a good candidate for spin-orbit localization because a face-centered-cubic lattice doesn't allow internal electric fields. However, plutonium clearly has a tendency to form complex lattices, and so internal electric fields could appear transiently. Of course internal electric fields can only appear in a conductor if the screening length is not too small, but plutonium is distinctive in having a very low conductivity.

A theory describing soliton-like localization for itinerant charge carriers that is applicable when the spin-orbit localization length is smaller than the screening length has been put forward by this author in a paper that will appear in *Philosophical Magazine*. The original motivation for this theory was to explain superconductivity in oxide materials such as  $Cd_2Re_2O_7$  and the hole-doped cuprates. In the case of the hole-doped cuprates, evidence that localized charge and spin fluctuations might

## PLUTONIUM AND QUANTUM CRITICALITY

be intimately associated with the occurrence of superconductivity is provided by evidence for a spin-glass phase in  $\text{LaCuO}_4$  doped with strontium.

Recently Christos Panagopoulos and Vladimir Dobrosavljevic have used muon spin rotation to show that the spin-glass phase in  $\text{LaCuO}_4$  doped with strontium extends all the way from zero hole doping to a hole doping near to optimal doping for superconductivity, i.e., roughly in the middle of the superconducting region. Thus it appears quite plausible that there is an intimate connection between the quantum fluctuations associated with the spin-glass phase and high- $T_c$  superconductivity. Of course, one may hesitate to claim that spin-orbit localization is responsible for the spin-glass phenomena in high- $T_c$  superconductors because it is difficult to justify why spin-orbit effects should be important in the cuprates. On the other hand, there is little doubt that such effects could be important in the actinides, and a theory of spin-orbit localization may be just what is needed to understand the quantum critical properties of plutonium.

Spin-orbit localization of charge carriers does not by itself imply that there is a gossamer condensate. However, it turns out that it is very natural for spin-orbit localized carriers with opposite spin to be paired, and one can explicitly write down the condensate wave function. Very recently direct evidence for the appearance in plutonium of a condensate that may be similar to the gossamer condensate in the high- $T_c$  cuprates has been provided by studies of the effect of alpha decay damage in plutonium on the magnetization carried out at Livermore by Fluss and McCall.

Both  $\alpha$  and  $\delta$  plutonium have large temperature-independent magnetic susceptibilities that increase with time at low temperatures. Isochronal annealing experiments show that these increases are connected with the radiation damage of the lattice. However,

the dominant contribution to the magnetic susceptibility at early times corresponds to an electronic bubble whose size is considerably larger than expected from quantum Monte Carlo calculations of the damage cascades. The temperature dependence of the susceptibility of these bubbles fits well to a Curie-Weiss law, with possibly a small Neel temperature, indicative of localized antiferromagnetic fluctuations. The occurrence of such bubbles is natural if one is near to a QCP like that shown in the figure on page 11. This would be a quantum analog of the familiar mixed phases that appear in classical gases near to their critical point.

I would like to close by exhibiting an exact solution to the nonlinear Schrödinger equation that describes the condensate ground state for the charge carriers in a three-dimensional layered conductor when the spin-orbit localization length is smaller than the screening length. This wave function describes a fluid of magnetic monopole-like carriers

$$\Psi = f(\bar{z}) \prod_{k>j}^{\infty} \left[ \frac{R_{jk} + U_{jk}}{R_{jk} - U_{jk}} \right]^{1/2},$$

where  $R_{jk}^2 = U_{jk}^2 + 4(z_j - z_k)(\bar{z}_j - \bar{z}_k)$ , and  $U_{jk} = U_j - U_k$  describes the distances between carriers using complex coordinates  $z_i$  within each plane, and  $f(\bar{z})$  is an analytic function of the  $\bar{z}_j$ . The function  $f(\bar{z})$  describes the natural tendency for the pairing of these charge carriers by virtue of the fact that magnetic monopoles with opposite magnetic charge attract

This work was performed in part under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.



## Postdoc's poster chosen for oral presentation

Eric Schelter had his poster selected for oral presentation at a Gordon Research Conference on Inorganic Chemistry in Newport, R.I. Being selected was an honor in itself because only four of 120 posters submitted were chosen for oral presentation. On top of that, Schelter was the only postdoc; the other three presenters were assistant professors up for tenure.

"It was a real thrill to stand up and talk in front of the demigods of inorganic chemistry," Schelter said.

Schelter received a doctorate in inorganic chemistry from Texas A&M University in 2004. He is in his second year of a Seaborg Institute postdoctoral appointment in Actinide, Catalysis, and Separations Chemistry (C-SIC) under the mentorship of Jaqueline Kiplinger.

"Eric did a superb job," said Kiplinger. "Lots of people were really impressed and commented accordingly."

Schelter's poster was titled "Covalency and Magnetic Communications in 5f-Element Complexes." Co-authors include Kiplinger, fellow postdoc Jacqueline Veauthier, student Kimberly Jantunen, Brian Scott, David Morris, Joe Thompson, and Kevin John, all of whom are members of Los Alamos' Chemistry or Materials Science Divisions.

The research focuses on how 5f orbitals in actinide ions may be involved in metal-ligand bonding, if involvement of these orbitals affects the properties of complexes of these ions, and if multimetallic complexes will exhibit metal-metal communication. The penultimate result was exciting, according to Schelter, and revealed a completely novel structure type: the first heterometallic 4f-5f complex. The complex serves as a discrete molecular unit that can be studied to detect short-range electronic and magnetic interactions in f-element complexes.

For this study, the researchers began by synthesizing eight uranium complexes with

slightly different structures and examining them to see what was happening between the uranium ion and ketimide ligands. The researchers found that there was a strong interaction between the uranium ion and the ligand in these complexes, which indicated a good electronic and magnetic pathway for communication.

Next, by hooking two metal ions together, in this case uranium and ytterbium, the complex was found to exhibit magnetic coupling, the first actinide-lanthanide compound to do so. Current research uses compounds containing one actinide and two lanthanide ions, but eventually the study will use multiple actinides. Lanthanides are being used as "stepping-stone" complexes because their electronic structures are relatively more simple than those of the actinides.

Schelter says the system the researchers have developed makes for interesting study because the lanthanide site on this molecule can be substituted with any lanthanide ion, which allows the researchers to expand their study and try a lot of different things.

The Gordon Conferences focus on new, unpublished research. Schelter is in the process of writing three papers based on the content of the poster. The research is one aspect of a Laboratory Directed Research and Development project in collaboration with Theoretical and Materials Science and Technology Divisions.

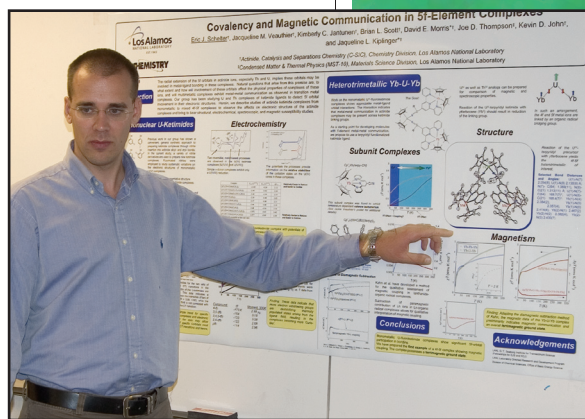
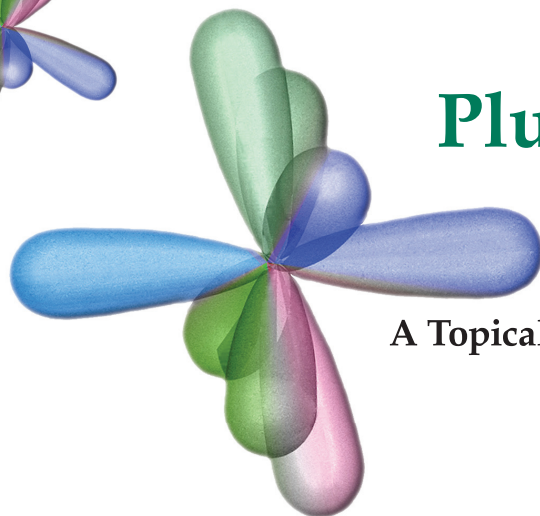
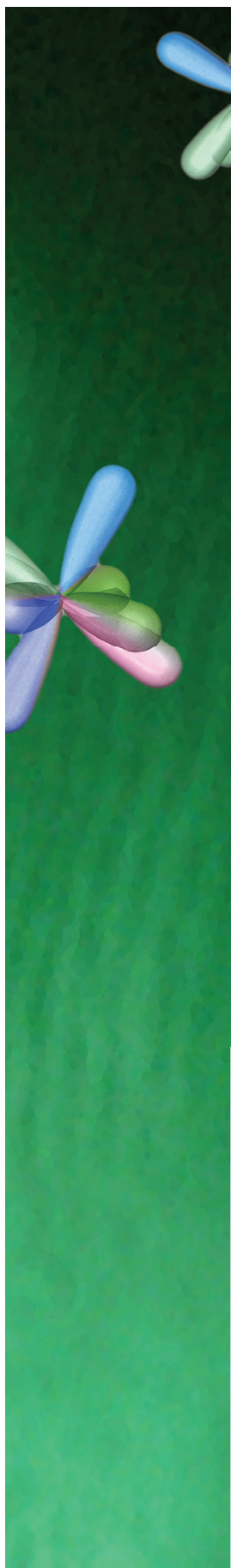


Photo by Dixon Wolf

*Postdoc Eric Schelter and his poster that was chosen for oral presentation at a Gordon Research Conference.*



# Plutonium Futures— The Science 2006

Pacific Grove, California

## A Topical Conference on Plutonium Actinides

The Plutonium Futures—The Science 2006 conference will be held July 9-13 in Pacific Grove, Calif. The conference, fourth in a series, will provide an international forum for presentation and discussion of the chemical and physical properties of plutonium and other actinides in complex media and materials. The conference also will focus on current and emerging sciences (chemistry, physics, materials science, nuclear science, and environmental concerns) of plutonium and actinides relevant to enhancing global nuclear security. The technical basis for addressing these important and timely issues requires intensive and increasing understanding of the underlying science and technology of plutonium and other actinides.

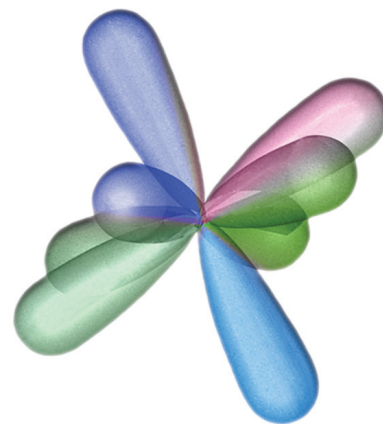
The Plutonium Futures—The Science conference was established to increase awareness of the importance of plutonium research and to facilitate communication among its international practitioners. U.S. and international scientists, engineers, faculty, and students from universities, national laboratories, and DOE's nuclear complex are encouraged to participate and make technical contributions. Most technical papers will be presented in one of three poster sessions. About eighty papers will be selected for oral presentation as plenary or invited papers. The deadline for submission of abstracts

is Feb. 15. Authors must register for the conference for their abstracts to be accepted. Additional details on submitting abstracts and a downloadable template are available on the website provided below.

Repeating a successful innovation introduced in the past two conferences, there will be a half-day introductory tutorial session on actinide science for students, non-specialists, and other interested parties on the afternoon of Sunday, July 9, before the official start of the conference. The tutorial will cover three topical areas that should be educational to those new to plutonium and actinide science. At the same time, the contemporary nature of the topics will also be of interest to "old-timers."

The previous conference, held in July 2003 in Albuquerque, N.M., attracted more than 350 people from sixty institutions and eighteen countries. Plutonium Futures—The Science 2006 is organized by Los Alamos and Lawrence Livermore National Laboratories and is co-sponsored by the American Nuclear Society. The registration deadline is May 15.

Additional information about the conference and registration and guidelines for submitting abstracts is available online at <http://www-cms.llnl.gov/pu2006>.



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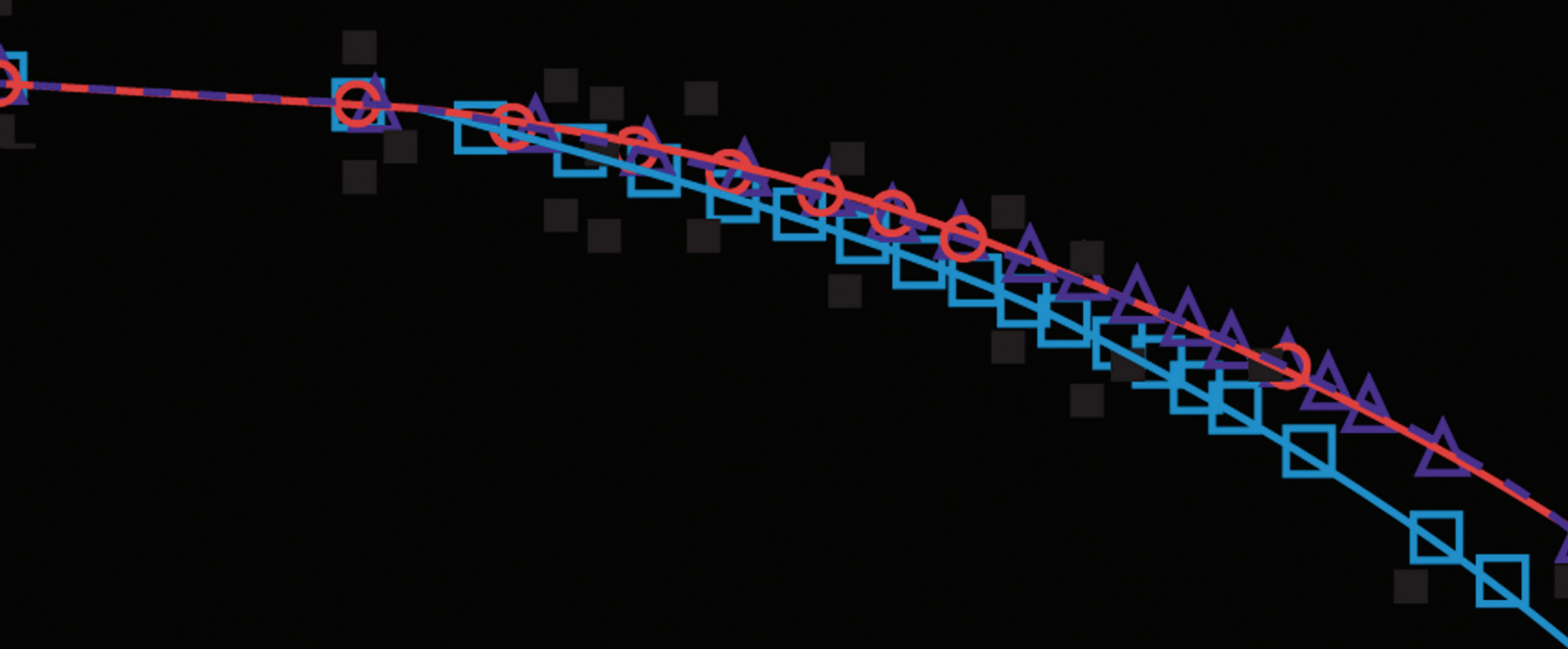
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