SYMPOSIUM DD

DD: Actinides-Basic Science, Applications, and Technology

December 1 - 3, 2003

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* Invited paper

SESSION DD1: Actinide Phase Stability, Transformations and Aging
Chair: Adam Schwartz
Monday Morning, December 1, 2003
Gardner (Sheraton)

NOTE EARLY START

8:25 AM OPENING REMARKS - JAMES TOBIN

8:30 AM *DD1.1
Plutonium: The Most Challenging Actinide. Siegfried S. Hecker, MST-DO, Los Alamos National Laboratory, Los Alamos, New Mexico.

Plutonium is of practical interest principally because the 239 isotope has attractive nuclear properties for energy production and nuclear explosives. It is plutonium's structural properties, however, which are determined by its electronic rather than its nuclear structure that are particularly unusual. Plutonium is notoriously unstable with temperature, pressure, chemical additions, and time. Its behavior defies conventional metallurgical wisdom. It exhibits huge volume changes in the solid state, primarily resulting from structural transformations among an unprecedented six solid allotropes. The ambient-temperature α-phase of plutonium is a low-symmetry monoclinic crystal lattice, more typical of minerals than of metals. The high-symmetry, close-packed face-centered cubic δ-phase exhibits the lowest density. The liquid is denser than the high-temperature solid phases resulting in contraction upon melting. The high-temperature fcc δ-phase exhibits an unusual negative thermal expansion coefficient and has the largest low-temperature specific heat of any pure element. It is also the most elastically anisotropic fcc element in the periodic table. The δ-phase can be retained to room temperature with the addition of a few atomic percent alloying elements such as aluminum or gallium. Such alloys also exhibit a low density. Their thermal expansion coefficients vary from slightly negative to slightly positive (an Invar-like effect) depending on alloying concentration and temperature. Their electrical resistivities are unusually large and increase on cooling below room temperature until $\sim$180K before decreasing rapidly as the temperature is furthered lowered. These alloys also exhibit a large low-temperature specific heat and an unusually large paramagnetic susceptibility, although no local moments have been found to date. These properties are all telltale signs of novel interactions and correlations among electrons, which typically result from a competition between itinerancy and localization. In the elements, we find that such novel interactions occur in the d and f electron metals near iron, at cerium, and near plutonium. Right at plutonium, the 5f electrons are caught in an abrupt transition between being bonding and being localized (chemically inert). The high-temperature, high-volume fcc δ-phase appears to be in a mixed state, being neither fully bonding nor fully localized. It has proven to be the most challenging phases to explain from first-principles calculations. I will describe the transformation behavior between the retained fcc phase and the monoclinic ground state at room temperature and below. These martensitic transformations trap solute atoms in metastable positions resulting in very peculiar volume effects and instabilities with time and temperature.

9:15 AM DD1.2
Synchrotron Diffraction Study of the Isothermal Oxidation of Uranium Dioxide at 250 C. Lionel Desgranges[2], Gurvan Rousseau[2,1,3], Jean-Claude Niepce[3], Jean-Francois Berar[4] and Gianguido Baldinozzi[1]; [1]SPMS, CNRS-Ecole Centrale Paris, Chatenay-Malabry, France; [2]DEN/DEC, CEA Cadarache,, St. Paul-lez Durance, France; [3]LRRS, CNRS-Univ Bourgogne, St. Paul-lez Durance, France; [4]ESRF, CNRS, Grenoble, France.

UO2 is the main material used in the fabrication of nuclear fuel elements. Its oxidation into U3O8 is of technological and academical interest because of the severe consequences during the nuclear fuel cycle. The structural mechanism responsible for the isothermal transformation of UO2 into U3O8 seems still unclear. Several phases (UO2+x, U4O9, alpha-U3O7, beta-U3O7, U3O8) were previously reported but their true structures and the boundaries between their existence domains are still a matter of discussion. In order to gather accurate structural information on the actual phases produced during an isothermal oxidation at 250 C, we have performed in-situ synchrotron X-ray diffraction experiments at ESRF. At this temperature, under ambient air, UO2 is found to transform into a faulted fluorite-like phase (U4O9) which is in turn transformed into a faulted tetragonal phase (beta-U3O7). After the recovery of its defects, this tetragonal phase is then transformed into an orthorhombic phase which is found to be U3O8. These experimental results do not support the previous evidence for an intermediate alpha-U3O7 single phase. These previous results are possibly related to a poor instrumental resolution, inducing a sensible broadening of the diffraction peaks. A microscopic model based on the new phase transition sequence for this low temperature isothermal oxidation mechanism is discussed.

9:30 AM DD1.3
Transformation crystallography and plasticity of the $\delta \rightarrow \alpha\prime$ transformation in plutonium alloys. Christopher R. Krenn, Mark A. Wall and Adam J. Schwartz; Lawrence Livermore National Laboratory, Livermore, California.

In delta-phase Pu-Ga alloys, the transformation from the ductile face-centered cubic delta phase that is retained at room temperature to the brittle low-temperature monoclinic alpha prime phase is a thermally activated diffusionless transformation with double-c kinetics. Accurate modeling of the phase transformation requires detailed understanding of the transformation path and the role of plastic flow during the transformation. Using transmission electron microscopy (TEM), we have confirmed the parallelism between alpha (020) and delta (111) planes and between alpha [100] and delta [110] directions seen previously, but, unlike earlier authors, who found a habit plane perpendicular to [123] in delta, we find that the habit plane is usually nearly perpendicular to [111] delta. Analysis of a variety of optical micrographs of partially transformed alloys is consistent with this observation. In alpha prime formed at low temperatures, TEM also shows very little apparent twinning within the alpha prime plates, but it does show that each plate is made up of alternating regions of two crystallographically unique variants, related by an approximately 60 degree rotation about [100] alpha. Finally, we find a significant increase in dislocation density in delta near the alpha prime plates, which suggests that plastic deformation contributes to the accommodation of the 20% reduction in volume during the transformation. These observations are used to validate new computational models of the $\delta \rightarrow \alpha\prime$ transformation. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

9:45 AM DD1.4
Experimental electronic heat capacities of α and δ Plutonium: heavy-fermion physics in an element. Jason Lashley, John Singleton, Jon Betts, Rob McQueeney, R.A. Fisher, Albert Migliori and James L Smith; MST-NHMFL, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have measured the heat capacities of δ-Pu (5% Al) and α-Pu over the temperature range 2-303 K. The availability of data below 10 K plus an estimate of the phonon contribution to the heat capacity based on recent neutron-scattering experiments on the same sample enable us to make a reliable deduction of the electronic contribution to the heat capacity of δ-Pu (5% Al); we find γ = 64 (3) mJ/K/mol/K as the temperature tends to zero. This is a factor of order 4 larger than that of any element, and large enough for δ-Pu to be classed as a heavy-fermion system. By contrast, γ = 17 (1) mJ/K/mol/K in αPu. Two distinct anomalies are seen in the electronic contribution to the heat capacity of δ-Pu (5% Al), one or both of which may be associated with the formation of the α' martensitic phase. We suggest that the large γ-value of δ-Pu may be caused by proximity to a quantum-critical point.

10:30 AM DD1.5
Investigations of Actinide Metals and Compounds Under Pressure Provide Important Insights into Bonding and Chemistry. Richard G. Haire[1], S. Heathman[2], Le Bihan[3], A. Lindbaum[4] and M. Iridi[2]; [1]CSD, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]European Commission, JRC, Institute for Transuranium Elements, Karlsruhe, Germany; [3]European Synchrotron Radiation Facility, Grenoble Cedex, France; [4]Vienna University of Technology, Institute for Solid State Physics, Wien, Austria.

One effect of pressure on elements and compounds is to decease interatomic distances, which can bring about dramatic perturbations in their electronic nature. The effect on the electronic configurations and the energies of different orbitals can result in bonding changes, which are reflected in physical and chemical properties. One important issue in the actinide series of elements is the effect on the 5f-electrons. We have probed changes in electronic behavior with pressure by monitoring structure, and studied several actinide metals and compounds from thorium through einsteinium under pressure via X-ray diffraction. These studies have employed synchrotron radiation and energy dispersive techniques via conventional X-ray sources. With actinide metals and alloys, their 5f-electrons are often affected significantly by pressure, while with the with the selected oxide and pnictide compounds the structural changes were not found to be linked to f-electron involvement. We shall present some of our more recent findings from studies of selected actinide metals, alloys and compounds under pressure. A discussion of the results in terms of the changes in electronic configurations and bonding with regard to the element's position in the series will also be included. [Research

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10:45 AM DD1.6
Low-Temperature Aging and Phase Stabiliy of U6Nb.
Luke L. Hsiung[1] and Clyde L. Briant[2]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Division of Engineering, Brown University, Providence, Rhode Island.

Aging behavior and phase stability of a water-quenched U-6wt.%Nb alloy artificially aged (AA) at 200°C for different periods of time (2, 4, 8, and 16 hours) and naturally aged (NA) at an ambient temperature for 15 years have been investigated using the Vickers hardness test and transmission electron microscopy (TEM) technique. The hardness of AA alloy samples initially increases from HV 190 (WQ) to HV 255 (200°C, 8h) and subsequently decreases to HV 237 (200°C, 16h). The observed age hardening/softening phenomenon can be rationalized by the occurrence of spinodal decomposition (i.e. the fine-scale of Nb segregation) within the AA samples. A modulated structure (presumably containing very fine domains of Nb-lean and Nb-rich phases) is first found within the parent (α'') phase at a very local region of the sample aged for 2 hours. The wavelength of the modulation (3 - 4 nm) is determined according to the spacing of satellite spots exited by the [001] modulation around the Bragg peaks. The modulation becomes more pronounced after aging for 8 hours, which results in the increase of hardness to a maximum. Further aging of the alloy causes the coarsening of segregated domains, and results in the decrease in hardness. The occurrence of order-disorder transformation is found within the NA alloy sample based upon the TEM observation of antiphase boundaries (APB/s). A possible crystal structure of an ordered α phase is proposed according to the comparison between observed and simulated diffraction patterns. It is suggested that the spinodal decomposition observed in the AA samples is the early stage of an ordering reaction. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. Work performed at Brown University was supported by Lawrence Livermore National Laboratory.

11:00 AM DD1.7
Crystallographic Anisotropy in Compression of Uranium Metal to 100 GPa.
Yogesh Vohra[1], J Reed Patterson[2] and Jagannadham Akella[2]; [1]Physics, University of Alabama at Birmingham, Birmingham, Alabama; [2]Lawrence Livermore National Laboratory, Livermore, California.

X-ray diffraction studies were carried out on Uranium metal of 99.9 % purity in a diamond anvil cell to 100 GPa at room temperature using synchrotron radiation with a variety of pressure markers like ruby, copper and platinum. The diffraction patterns are carefully indexed allowing for reversal of peak positions based on anisotropic compression. We report anisotropic compression of the orthorhombic unit cell with the axial ratio b/a increasing rapidly to 40 GPa followed by a rapid decrease at higher pressure. On the other hand, axial ratio (c/a) shows a rapid increase with increasing pressure followed by a saturation at megabar pressure. Overall, c-axis is the least compressible and the b-axis is the most compressible in the orthorhombic unit cell. The observed anisotropic compression is correlated with the changes in the 5-f bonding and electrostatic interactions in the alpha-Uranium phase. This research is supported by the Department of Energy (DOE) Grant No. DE-FG03-03NA00067/A000.

11:15 AM DD1.8
Investigating the δ/α' Phase Transformation in Pu-Ga Alloys.
Kerri J.M. Blobaum, Jeffery J Haslam, Mark A Wall and Adam J Schwartz; Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California.

The δ to α' phase transformation in Pu-Ga alloys is intriguing for both scientific and technological reasons. On cooling, the ductile fcc δ-phase transforms martensitically to the brittle monoclinic α'-phase at ~160 K (depending on composition). This exothermic transformation involves a 20% volume contraction and a significant increase in resistivity. Complete transformation to the a' phase is not observed; typically a maximum of 30% is formed. Furthermore, time-temperature-transformation diagrams found in the literature indicate that the kinetics of this transformation involve "double-C-curve" behavior, and the two maximum rates of transformation are a function of composition. The reversion of α' to δ involves a large temperature hysteresis; reversion begins at ~310 K. In an attempt to better understand the underlying thermodynamics and kinetics responsible for these unusual features, we examined the α'/δ transformations in a 0.6 wt% Pu-Ga alloy using differential scanning calorimetry, resistometry, transmission electron microscopy, and optical microscopy. At this composition, the martensite start temperature is ~154 K and the austenite start temperature is ~310 K. Differential scanning calorimetry shows evidence of α' formation and reversion to δ. The feature corresponding to the reversion contains a series of "oscillations" which are the subject of much investigation. These "oscillations" are periodic, and their periodicity with respect to temperature does not vary with heating rate. Furthermore, the alloy exhibits a rather unique transformation behavior that is dependent on time at room temperature. Possible reasons for these observations will be discussed. Elucidating the thermodynamics and kinetics of the δ/α' phase transformation are important for understanding how Pu-Ga alloys can change over time and under a variety of thermal conditions. Basic studies such as this provide the scientific framework for future work in the area of stockpile stewardship. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

11:30 AM DD1.9
Local Structure, Inhomogeneities, and Structural Properties of f-electron Solids.
Rafael Howell, Angel Garcia-Adeva and Steven D. Conradson; Materials Science and Technology Division, Los Alamos National Laboratorz, Los Alamos, New Mexico.

Many f-electron solids, e.g., plutonium alloys and oxides, etc., exhibit intentional or inadvertent deviations of their chemical formulas from their unit cell stoichiometries and therefore contain inhomogeneities at concentrations ranging from one up to several dozen atom-%. In many cases these inhomogeneties act collectively to organize into non-diffracting, aperiodic, nanoscale domains whose atoms are differently ordered than the host lattice. These observations pose the question of how the atoms are actually arranged in the material on all length scales from that of atoms on up and what are the resulting structure:property relationships that endow them with compelling transformational and chemical properties. These phenomena and their ramifications have been explored with semi-empirical calculations that begin with the observed local structure characteristics and subsequently determine the resulting structure factors and electronic structure properties. An effort has also been initiated to understand the energetics and the means by which such heterogeneous structures can be stabilized. As an example, we have found that the most fundamental microscopic elastic property, the linear relationship between composition and lattice constant known as Vegard's Law, may require cooperative action between inhomogeneity sites and thus be a many body phenomenon rather than a simple manifestation of difference in atomic size. We also have indications that the interfaces between internal domains may have unique electronic structures that can carry over to the bulk.

11:45 AM DD1.10
Density Changes in Plutonium Observed from Accelerated Aging using Pu-238 Enrichment.
Brandon W. Chung, Stephen R Thompson, Conrad H Woods, David J Hopkins, William H Gourdin and Bartley B Ebbinghaus; Lawrence Livermore National Laboratory, Livermore, California.

Plutonium, because of its radioactive nature, ages from the "inside out" by means of self-irradiation damage and thus produces Frankel-type defects (vacancies and self-interstitial atoms) and defect clusters. The self-irradiation damage in Plutonium-239 occurs mainly by α-particle decay, where most of the damage comes from the U-235 recoil nucleus. The defects resulting from the residual lattice damage and helium in-growth could result in microstructural and physical property changes, which are of interest to the Stockpile Stewardship Program. Because these self-irradiation effects would normally require decades to measure, with a fraction (7.5 wt%) of Pu-238 is added to the weapons-grade plutonium thus accelerating the aging process by 16 times the normal rate. By monitoring the properties of the Pu-238 spiked alloy over a period of about 3.5 years, the properties of plutonium in stockpile pits can be projected for periods up to about 60 years. This paper presents density and volume changes observed from the immersion density and dilatometry measurements equivalent to aging weapons-grade plutonium to nine years. The increase in sample length at 35, 50, and 65°C storage temperature as a result of self-irradiation follows exponential dependence on dose or time during initial stage of aging. After three equivalent years of aging, the samples at 35°C have elongated by 0.02% and start to exhibit a near constant value. The changes in lattice parameters determined by X-ray diffraction method are also presented. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48

SESSION DD2: Phononic and Electronic Structure
Chair: John Joyce
Monday Afternoon, December 1, 2003
Gardner (Sheraton)

1:30 PM *DD2.1
Electronic Structure of Plutonium: A Dynamical Mean Field Approach. Gabriel Kotliar[1] and sergej savrasov[2]; [1]physics, rutgers university, piscataway, New Jersey; [2]physics, NJIT, Newark, New Jersey.

The unusual properties of elemental plutonium, results from the proximity of the f electron to a localization delocalization transition (Mott transition). Dynamical mean field theory (DMFT) is a new electronic structure method, which has given a new understanding of this Mott transition regime. In this talk, we will describe results of the application of this method to the delta phase and the epsilon phase of Plutonium. We will discuss new qualitative insights into the anoalous properties of plutonium. DMFT has also been used to obtain quantitative results and we will present results for the total energy, the photoemission spectra and the phonon spectra of Plutonium, and compare them to experiments.

2:00 PM *DD2.2
Experimental Phonon Dispersion Curves of Gallium-Stabilized fcc d-Plutonium by Inelastic X-ray Scattering. Joe Wong[1], M. Krisch[2], D. Farber[1], F. Occelli[1], A. J. Schwartz[1], M. Wall[1], R. Xu[3] and T.-C. Chiang[3]; [1]CMS, LLNL, Livermore, California; [2]ESRF, Grenoble, France; [3]U. Illinois, Urbana-Champaign, California.

Plutonium is arguably the most complex metallic element known, and has attracted extraordinary scientific interest since its discovery in 1941. Further, detailed understanding of the properties of plutonium and plutonium-based alloys is critical for the safe handling, utilization, and long-term storage of these important, but highly toxic, materials. However, both technical and safety issues have made experimental observations extremely difficult. Here, we report an experimental determination of the phonon dispersion curves in a face-centred cubic (fcc) d plutonium-0.6 wt% gallium alloy. Our results show several unusual features including a profound elastic anisotropy, an exceptionally small shear elastic modulus C', a Kohn-like anomaly in the T1[011] branch, and a pronounced softening of the [111] transverse modes. These features can be related to the phase transitions of plutonium and to strong coupling between the lattice structure and the 5f valence instabilities. Our results also provide a critical test for theoretical treatments of highly correlated 5f electron systems as exemplified by recent dynamical mean field theory (DMFT) calculations for d-plutonium. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

2:30 PM DD2.3
Uranium Phonons Measured at High Temperatures with Inelastic Neutron and X-ray Scattering Reveal a Pervasive Coupling of Electron and Phonon Degrees of Freedom. Michael Edward Manley[1], Gerry Lander[2], Harald Sinn[3], Jason Lashley[1] and Ahmet Alatas[3]; [1]Los Alamos National Laboratory, Los Alamos, New Mexico; [2]European Commission, JRC, Institute for Transuranium Elements, Karlsruhe, Germany; [3]Argonne National Laboratory, Argonne, Illinois.

When heated from room temperature up to 940 K the phonon density of states (DOS) of uranium softens by an order of magnitude more than what is expected from its thermal expansion [1]. A more detailed analysis of the vibrational spectra shows that the interatomic potential softens while remaining harmonic. The lack of anharmonicity implies that the interatomic potential landscape of uranium is greatly altered by electronic excitations as the temperature is raised [1]. A further implication is that thermal electronic excitations alter phonon entropy. The effect of this extra phonon entropy is to stabilize electrons to energies beyond that given by the usual Fermi distribution and thermodynamic properties are also significantly enhanced [2]. In order to obtain a deeper understanding of the mechanism(s) behind this unusual behavior we mapped out the temperature dependence of a few key phonon branches using high resolution inelastic X-ray scattering at the Advanced Photon Source. Preliminary results show that some phonon branches become lifetime broadened over a narrow temperature range (< 50 K around 425 K) with a subsequent redistribution of intensity between essentially fixed frequency branches. [1] M. E. Manley, B. Fultz, R. J. McQueeney, C. M. Brown, W. L. Hults, J. L. Smith, D. J. Thoma, R. Osborn, and J. L. Robertson, Phys. Rev. Lett. 86, 3076 (2001). [2] M. E. Manley, Phil. Mag., 83, 2467 (2003).

2:45 PM DD2.4
Nuclear Magnetic Resonance Studies of δ-Plutonium. Nicholas Curro, Condensed Matter and Thermal Physics, Los Alamos National Laboratory, Los Alamos, New Mexico.

We present Knight shift and spin lattice relaxation data in Gallium stabilized δ-Plutonium as a function of temperature. The dominant hyperfine interaction experienced by the Ga nuclei is a contact interaction with the conduction electrons. By measuring the shift and relaxation rates, one can probe properties of the Fermi surface. Deviations from Korringa behavior often reveal the presence of strong correlations. LAUR 03-3995

3:30 PM *DD2.5
VUV and Soft X-Ray Spectroscopy of Actinides. Clifford G. Olson, Ames Laboratory, Iowa State University, Ames, Iowa.

Optical and photoelectron spectroscopies using VUV and Soft x-ray photons are powerful tools for studies of elemental and compound actinides. Large changes in the relative atomic cross sections of the 5f, 6d and sp electrons allow decomposition of the character of valence bands using photoemission. Resonant enhancement of photoelectrons and Auger electrons at the 5d core threshold further aid the decomposition and give a measure of elemental specificity. Angle resolved photoemission can map the momentum dependence of the electronic states. The large changes in relative cross section with photon energy yields further details when the mapping is done at equivalent points in multiple zones. High resolution angle-resolved photoemission at low temperatures is a powerful technique for Fermi surface mapping. USb2 will be one of the examples discussed. ARPES on excellent single crystals shows a very narrow peak (<5mev natural width) of mixed U f-d character with a binding energy of 40 meV at zone center. Away from the zone center, the state disperses towards the Fermi level before splitting and moving deeper. With increasing temperature, this state changes, a result of a transition subsequently seen in bulk susceptibility and resistivity measurements. Comparisons will be made between the Cerium and Uranium analogs of the 115 and 218 compounds. * In Collaboration with the Los Alamos National Laboratory team of J.J. Joyce, T. Durakiewicz, M.T. Butterfield, E. Guziewicz, and J.L. Sarrao

4:00 PM *DD2.6
Failure of Russell-Saunders Coupling in the 5f States of Plutonium. Kevin Thomas Moore[1], Mark A Wall[1], Adam J Schwartz[1], Brandon W Chung[1], David K Shuh[2], Roland K Schulze[3] and James G Tobin[1]; [1]Chemistry and Materials Science, Lawrence Livermore Nationa Labs, Livermore, California; [2]Chemistry and Materials Science, Lawrence Berkeley National Labs, Berkeley, California; [3]Chemistry and Materials Science, Los Alamos National Labs, Los Alamos, California.

The nature of Pu 5f electronic structure is still under debate [1-6]. Many of the complications are derived from the necessity of explaining the phase-specific behavior of Pu and Pu alloys, particularly the low-symmetry monoclinic alpha phase and the high-symmetry fcc delta phase. Experimentally, there are severe impediments, such as the present inability to grow large single crystals and the radioactive and chemical hazards of the materials. Theoretically, electronic structure calculations that have turned out reliable for all other metallic systems have failed for Pu because the 5f electrons are on the borderline between localized and itinerant behavior. Recent advances, including the application of dynamical mean-field theory (DMFT) to delta-Pu [2] and generalized gradient approximation (GGA) to delta-Pu [3] and to alpha- and delta-Pu [4], have begun to pave the way to better understanding of Pu 5f electronic structure. However, despite these efforts [7], there is still a considerable lack of experimental data to support assumptions made in the computational framework. One of these critical issues is the degree to which the interaction of the spin and orbital angular momenta in the 5f states must be included in such calculations. Here we use high energy electron energy loss spectroscopy (HE-EELS), transmission electron microscopy (TEM), and synchrotron-radiation-based X-ray absorption spectroscopy (XAS), to provide the first experimental evidence that Russell-Saunders (LS) coupling fails for the 5f states of Pu [8]. These results support the assumption that there is considerable spin-orbit splitting of the occupied and unoccupied 5f states of Pu. Therefore, only the use of jj or intermediate coupling is appropriate for the 5f states of Pu and spin-orbit splitting can not be neglected in the Hamiltonian for the 5f states of Pu and the other actinides. HE-EELS experiments were performed in a TEM and are coupled with image and diffraction data, therefore, the measurements are completely phase specific. References [1] R.C. Albers, Nature 410, 759 (2001). [2] S.Y. Savrasov, G. Kotliar, and E. Abrahams, Nature 410, 793 (2001). [3] S.Y. Savrasov and G. Kotliar, Phys. Rev. Lett. 84, 3670 (2000). [4] P. Soderlind, Europhys.

Lett. 55, 525 (2001). [5] H.L. Skrivers, O.K. Andersen, and B. Johansson, Phys. Rev. Lett. 41, 42 (1978). [6] B. Johansson, Phys. Rev. B 11, 2740 (1975). [6] S.S. Hecker, D.R. Harbur, and T.G. Zocco, Prog. Mat. Sci., in press; Challenges in Plutonium Science, Vol. I and II, Los Alamos Science, Number 26, LANL, 2002. [7] Cooper et al. Hybridization-induced anisotropy in cerium and actinide systems. in Handbook on the physics and chemistry of the actinides, ed. A.J. Freeman and G.H. Lander, Elsevier Science, Vol. 2, 1985. [8] K.T. Moore et al. Phys. Rev. Lett. 90, 196404 (2003).

4:30 PM DD2.7
Photoemission studies of the electronic structure of AnSb and AnTe single crystals (An = U, Np, and Pu).
Tomasz Durakiewicz[1], Martin T Butterfield[1], Ela Guziewicz[1], John J Joyce[1], Luis A Morales[1], Aloysius J Arko[1], Clifford G Olson[2], Gerry H Lander[3], Franck Wastin[3], Jean Rebizant[3], Oscar Vogt[4] and Kurt Mattenberger[4]; [1]MST Division, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Ames Laboratory, Iowa State University, Ames, Iowa; [3]Institute for Transuranium Elements, European Comission, Karlsruhe, Germany; [4]Laboratorium fur Festkorperphysik, ETH, Zurich, Switzerland.

We have performed photoemission (PES) experiments on the laser-cleaned surfaces of single crystals of the AnSb and AnTe series utilizing three different PES techniques. We have used: (i) a gas discharge lamp and angle-integrated PES using both HeI (21.2 eV) and HeII (40.8 eV) excitation lines, (ii) the laser plasma light source (LPLS) giving energies in the range 40 to 80 eV in angle-integrated mode, and (iii) utilizing synchrotron radiation in the range of 15 to 120 eV photon energy in the angle resolved mode of PES. This extends earlier work [1] reported on NpAs and, together with results from USb and UTe [2, 3], allows us to study the systematics of the electronic structures of these compounds. In all cases there is at least one strong peak in the photoemission spectra that can be identified from its energy dependence as associated with the main spectral weight of the 5f states. The distance of this peak from the Fermi energy (EF) all in eV is: USb 0.2; NpSb 0.7; PuSb 1.7; UTe 0.8; NpTe 1.3; PuTe $<$ 0.1. The compound that shows the greatest localization is therefore PuSb, and the most unusual is PuTe (also the only non-magnetic compound in this group), where there are at least three peaks within the first 1.2 eV below EF. The results for PuTe and PuSb agree well with those published [4] for PuSb and PuSe using thin films. This indicates that the spectral features are independent of the cleaning or surface preparation technique. The energy dependence, established by using the LPLS, also confirms that all Pu features within 2 eV of EF have a predominant 5f character [5]. We see a direct correlation between binding energy of 5f related peaks and magnetic transition temperature. This work was supported by the Department of Energy, Office of Science, Division of Materials Science and Engineering. References: [1] A. J. Arko et al., Phys. Rev. B 62, 1773 (2000). [2] B. Reihl et al., Phys. Rev. B 26, 1842 (1982). [3] H. Kumigashira et al., Phys. Rev. B 61, 15707 (2000). [4] T. Gouder et al., Phys. Rev. Lett. 84, 3378 (2000). [5] T. Durakiewicz et al., Phys. Rev. B submitted (2003).

4:45 PM DD2.8
Electronic Structure and Surface Science of delta Plutonium.
Martin Thomas Butterfield[1], Tomasz Durakiewicz[1], Ela Guziewicz[1], John J Joyce[1], Dave P Moore[2], Aloysius J Arko[1] and Luis A Morales[2]; [1]MST-10, LANL, Los Alamos, New Mexico; [2]NMT-16, LANL, Los Alamos, New Mexico.

We have investigated the electronic structure of delta plutonium using photoelectron spectroscopy (PES). The sample was cleaned by laser ablation. This method provided a demonstrably clean sample surface. With the sample free of contamination and the surface reproducible, we had an optimum arrangement for controlled gas dosing studies using O2 and H2. Results for adsorbate studies on Pu metal are used to correlate the electronic structure with surface reactivity. Investigations were carried out on the formation of the PuO2, and P2O3 oxides at the delta Pu surface with increasing O2 exposure (quantified in Langmuirs). The PES data, with an instrument resolution of 60 meV and a sample temperature of 77K, strongly supports the model of Pu2O3 growth at the metal surface and then PuO2 growth on the Pu2O3 layer. Over time the PuO2 reduces to Pu2O3 even at room temperature in ultra high vacuum with a base pressure of 6x10-11 Torr. The effects of hydrogen on the valence band electronic structure were also investigated. The PES data show an initial reduction of the peak at the Fermi level after a 5 Langmuir exposure, the appearance of a hydrogen-induced feature $\sim$6 eV below the Fermi level, and no substantive changes in the main 5f states between a binding energy of -0.5 and -2 eV. With additional H2 exposures (10L to 50L), the intensity of the peak at the Fermi level is reduced, the 6 eV peak intensity shows no change and the main 5f manifold is primarily invariant. Data will also be presented to show the effects of H2 dosing on top
of PuO2 and Pu2O3. Work supported by the US Department of Energy.

SESSION DD3: Actinides and the Environment
Chair: Lynda Soderholm
Tuesday Morning, December 2, 2003
Gardner (Sheraton)

8:30 AM *DD3.1
Actinides in the Environment. Teresa Fryberger[1] and Henry Shaw[2]; [1]Office of Biological and Environmental Research, Washington, District of Columbia; [2]LLNL, Livermore, California.

As the Department of Energy proceeds with its cleanup of environmental contamination resulting from nuclear weapons production and testing and as it proceeds with nuclear energy development, it becomes increasingly clear that there is still much to be learned about the behavior of actinides in the environment. It is essential that we develop the ability to make realistic predictions regarding the transport behavior of actinides in the environment. However, there are significant gaps in both data and process-level understanding that limit the accuracy and applicability of our models. Filling these gaps will require detailed understanding of the complex interactions of actinide solutions with oxide and other solid surfaces in the environment, as well as the effects of biological activity on these interactions. In addition, new materials for immobilization of actinides are needed both as waste forms and subsurface barriers. Finally, future uses of actinides will require the development of new processes and waste management approaches. For example, novel materials will be needed for separations of actinides from process streams and waste waters, for immobilization of actinides and daughter products, and for radioanalytical sensors. This presentation will discuss these needs and provide examples of research on these problems.

9:00 AM *DD3.2
Advances In Understanding Of The Crystal Chemistry Of Hexavalent Uranium. Peter C. Burns, Department of Civil Engineering and Geological Sciences, Uiversity of Notre Dame, Notre Dame, Indiana.

Research into the crystal chemistry of hexavalent uranium (uranyl) by the Environmental Mineralogy and Crystal Structures research group at Notre Dame has resulted in the description of more than 110 new structures of uranyl compounds (including 36 minerals). New insights into the crystal chemistry of uranium will be discussed in this presentation, with emphasis on recently discovered novel structural connectivities. The structural hierarchy of uranyl minerals and compounds, which was first established for 180 structures by Burns et al. in 1996, has been extended to include more than 130 new structures. The hierarchy, which is based upon polymerization of polyhedra of high bond-valence, involves five distinct classes: structures containing isolated uranyl polyhedra (7), finite clusters of polyhedra (34), chains of polyhedra (52), sheets of polyhedra (172), and frameworks of polyhedra (47). The dominance of sheets in uranyl compounds (55% of more than 310 known structures) arises from the unequal distribution of bond-valences within the uranyl polyhedra. Topological relations of the sheets in uranyl compounds is best understood by analysis of the topological distribution of anions within sheets in which sharing of polyhedral edges dominates, and by graphical representation of the connectivity of polyhedra in cases where sharing of vertices of polyhedra dominates the sheet.

9:30 AM DD3.3
X-ray Absorption Fine Structure Studies of Technetium Speciation in Borosilicate Glasses. Wayne Lukens[1], David Shuh[1], Isabelle Muller[2] and David McKeown[2]; [1]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Vitreous State Laboratory, The Catholic University of America, Washington, District of Columbia.

Technetium, a long-lived (^{99}Tc: 213,000 year half-life) fission product found in nuclear waste, is one of the important isotopes of environmental concern due to its high yield (6% of ^{235}U fission) and the environmental mobility of pertechnetat, TcO_4^-. In addition, technetium presents challenges to incorporation into waste matrices due to the thermodynamic stability of Tc(VII) and the presence of volatile technetium species, especially Tc_2O_7 and $CsTcO_4$, which can be lost during vitrification of glass waste forms. The identities of the technetium species actually retained in glasses following vitrification under conditions similar to those used to produce actual borosilicate waste glasses are not well known. Technetium containing borosilicate glasses have been prepared on the laboratory scale by vitrification of glass precursors and technetium containing waste simulants similar to the high level nuclear waste at the Hanford site. The speciation of technetium in glasses has been examined using X-ray absorption fine structure (XAFS) spectroscopy. The species found in the glass is

either Tc(VII) or Tc(IV) depending upon the components of the waste simulants, especially organic compounds.

9:45 AM DD3.4
Synthesis, Characterization, Sintering and Leaching of Thorium-Uranium (IV) Phosphate-Diphosphate Solid Solutions From Low-Temperature Precursors.
Nicolas J. Dacheux[1], Nicolas Clavier[1], Renaud Podor[2] and Philippe Le Coustumer[3]; [1]Radiochemistry Group, Nuclear Physics Institute, ORSAY, France; [2]LCSM, University H. Poincare-Nancy I, Vandoeuvre-Les-Nancy, France; [3]CDGA, University of Bordeaux I, Talence, France.

Phosphate matrices and especially uranium and thorium compounds present several properties of interest to immobilize tetravalent actinides. In this field, Thorium Phosphate-Diphosphate (TPD) was extensively studied in the last decade. Its structure allows the replacement of large amounts of thorium by uranium (IV), neptunium (IV) and plutonium (IV). These solids were prepared through a dozen ways of synthesis involving wet and dry chemistry methods. In order to improve the homogeneity of solid solutions, a new chemical route based on the preparation of a low-temperature well-crystallized precursor was developed. Several compositions of Thorium-Uranium (IV) Phosphate-Diphosphate (TUPD) precursor were synthesized in closed PTFE containers either in autoclave or on a sand bath. All the samples were chemically analyzed through PIXE and EPMA then characterized by XRD, IR and UV-Visible spectroscopies, SEM, TEM... From XRD data, it appeared that all diffraction lines matched well with that of Thorium Phosphate-Hydrogenphosphate and that a complete solid solution was obtained between pure thorium and uranium compounds. Low-temperature precursors appeared to be stable up to about 900°C. Above this temperature, its transformation into TUPD solid solution was observed for substitution rates U/(U+Th) lower than 0.7. The transformation was complete at 1000°C and well crystallized, homogeneous and single phase TUPD solid solutions were obtained. For higher substitution rates, a mixture of TUPD, uranium (IV) diphosphate and diuranium oxide phosphate was prepared. An accurate value (about 930°C) of the transformation temperature was given from TGA and DTA experiments. TUPD sintered samples were prepared by this way after a two-step procedure (uniaxial pressing at room temperature then heating treatment at 1250°C). Dilatometric study revealed that the sintering occurred between 1000°C and 1250°C. The apparent and effective relative densities were determined using helium and water pycnometries then the open and close porosities were evaluated. Complete characterization and observation was also developed on these pellets. Chemical durability of either powdered or sintered TUPD samples was examined in several media. The multiparametric expression of the normalized dissolution rate was proposed in acidic and basic media. All the normalized dissolution rates were found to be very low, demonstrating the good retention properties already described for TPD. From this study, it appeared that thorium was quickly precipitated at the surface of the sample as thorium phosphate while uranium (in the uranyl form) remained in the leachate. The complete characterization of all these low-soluble neoformed phases is now under progress.

10:30 AM DD3.5
Thermal- and Radiation Induced Chemistry of Water on UO_2 Surfaces. Jeffrey A. Stultz, Stephen A. Joyce and Mark T. Paffett; Los Alamos National Lab, Los Alamos, New Mexico.

Most plans for the disposition of surplus nuclear materials involve storage in sealed containers where the evolution of gases from reactions of adsorbed water could present both pressure and flammability hazards. To better understand the relative importance of the thermal- and radiation-induced chemistry, we have studied the interactions of water on single crystals of uranium dioxide. Temperature programmed desorption and electron stimulated reaction/desorption are used to examine the chemistry. In the absence of radiation, water adsorbs/desorbs molecularly on "pristine" oxide surfaces with a binding energy of only a few kcal/mole greater than water with itself. The strength of this interaction is large enough to indicate that UO_2 surfaces handled outside the driest of environments will be covered with water. External low energy electron irradiation is used to simulate the effects of radiolytic chemistry induced by decay particles. The principle neutral gaseous radiolytic products are H_2, O_2, and water. The relative yields are strongly dependent on temperature and coverage. The electron stimulated desorption of ions, which is often sensitive to minority species, indicates that surface hydroxyls, presumbaly formed at defects, are stable up to moderately high temperatures ($\sim$ 600K). To further elucidate the role of surface defects on the interactions of water with uranium dioxide surfaces, thier concentration was increased purposefully using ion sputtering. Evidence suggests water adsorbs dissociatively at defective surface sites, leading to hydrogen gas formation upon annealing.

10:45 AM DD3.6
Study of Actinides Incorporation in Thorium-Phosphate Diphosphate/Monazite Based Ceramics. Nicolas Clavier[1], Nicolas Dacheux[1], Renaud Podor[2] and Philippe Le Coustumer[3]; [1]Radiochemistry Group, Nuclear Physics Institute, Orsay, France; [2]LCSM, University H. Poincare-Nancy I, Vandoeuvre-les-Nancy, France; [3]CDGA, University of Bordeaux I, Talence, France.

In the field of radwaste storage in an underground repository, Thorium Phosphate-Diphosphate (TPD) and Monazite are usually proposed as potential matrices, especially for the immobilization of actinides. On this basis, the elaboration of TPD/Monazite based ceramics was developed in order to incorporate simultaneously tri- and tetravalent actinides and neutron absorber (like gadolinium) in the eventuality of plutonium storage. Powdered samples were synthesized by wet (initial preparation of precursors for each phase at 150°C) and dry (mixing of TPD precursor and monazite) chemistry methods. U(IV) was first used as a surrogate of Pu(IV) in the TPD structure. Dense pellets were prepared from a two-step procedure involving uniaxial pressing at room temperature (100-500 MPa) then heating treatment at 1100-1250°C. The samples were extensively characterized by conventional techniques (SEM, TEM, XRD, EPMA...). At high temperature, the solids were always composed by two well crystallized phases. The first one was identified as Thorium-Uranium(IV) Phosphate-Diphosphate (TUPD) solid solution while the second one corresponded to Monazite. The geometrical density of the pellets usually reached 90-95% of the calculated value while the open porosity was evaluated to 1-6%. Several physico-chemical properties such as Vickers hardness, specific surface area... were also determined. The chemical durability of powdered and sintered samples was examined by making leaching tests in several media (acidic, basic or natural waters). The normalized dissolution rates were determined for thorium, uranium and rare earth. They were always low by comparison to other ceramics studied in the same aim for each element considered (including plutonium). The phases neoformed at the leachate saturation were identified then characterized. They were always phosphate-based phases and exhibited very low solubility products which could delay significantly the migration of radionuclides to the biosphere.

11:00 AM DD3.7
The impact of Au^{2+}-ion beam irradiation on the tetragonal distortion in the TiO_6 of $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$ single crystals: A Ti 2p and O 1s NEXAFS study.
Ponnusamy Nachimuthu[1,2], Suntharampillai Thevuthasan[3], William J Weber[3], Vaithiyalingam Shutthanandan[3], Yanwen Zhang[3], David K Shuh[1], Dennis W Lindle[2], Geetha Balakrishnan[4], Don M Paul[4], Eric M Gullikson[1] and Rupert C C Perera[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Chemistry, University of Nevada-Las Vegas, Las Vegas, Nevada; [3]Pacific Northwest National Laboratory, Richland, Washington; [4]Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom.

Pyrochlore is one of several candidate materials proposed for the immobilization of actinide-rich wastes including plutonium. The pyrochlores under consideration exhibit $A_2B_2O_7$ stoichiometry, where actinides and lanthanides are incorporated in the A-site and Ti or Zr occupy the B-site. Near edge x-ray absorption fine structure (NEXAFS) investigations of $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$ single crystals were carried out prior to and following 2.0 MeV Au^{2+} ion beam (dose $\sim 5.0 \times 10^{14}$ Au^{2+}/cm^2) irradiation. Prior to irradiation, the Ti L-edge NEXAFS show that Ti^{4+} ions in both $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$ occupy octahedral sites with a tetragonal distortion, which is induced by the vacant 8a oxygen sites located in the ab plane adjacent to TiO_6 octahedron. However, the magnitude of tetragonal distortion in the TiO_6 octahedron differs between $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$. The difference in the distortion between $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$ allows the determination of the relative disorder, which influences the radiation tolerances in these materials. Ion beam irradiation results in a phase transformation from the ordered pyrochlore structure ($Fd3m$) to the defect fluorite structure ($Fm3m$) and eventual amorphization of both of $Sm_2Ti_2O_7$ and $Gd_2Ti_2O_7$.

11:15 AM DD3.8
Elaboration, characterization and sintering of britholites doped with tetravalent actinides. Olivier Terra[1], Nicolas Dacheux[1], Fabienne Audubert[2], Christophe Guy[2] and Renaud Podor[3]; [1]Radiochemistry Group, Nuclear Physic Institute, Orsay, France; [2]DEN/DED/SEP/LCC, CEA Cadarache, Saint Paul Lez Durance, France; [3]LCSM, University H. Poincare-Nancy I, Vandoeuvre-les-Nancy, France.

Due to a rather high natural occurrence and a good resistance to radiation damage, neodymium substituted britholite $Ca_9Nd(PO_4)_5(SiO_4)F_2$ was already considered as a potential host

matrix for the specific immobilization of actinides. This formula was first optimized for the incorporation of trivalent actinides. The incorporation of tetravalent actinides like Th or U(IV) or of Ce (IV) in the structure was examined through the elaboration of $Ca_9Nd_{1-x}An(IV)_x(PO_4)_{5-x}(SiO_4)_{1+x}F_2$ samples. This study was the early beginning of the incorporation of ^{239}Pu and/or ^{238}Pu in order to evaluate the effects of α-decay on the britholite structure. Samples were prepared through dry chemistry methods involving an initial mixture of Nd_2O_3 / CaF_2 / ThO_2 or UO_2 / $Ca_2P_2O_7$ / SiO_2 / $CaCO_3$. In order to optimize the synthesis and the homogeneity of the solids, the mixtures were mechanically ground in a crusher, before heating at high temperature (1400°C). The solids were extensively characterized using several techniques (XRD, SEM, EPMA, XPS and EXAFS). The results showed that the incorporation of thorium in britholite structure was successful up to 10 Wt.%. The samples were always homogeneous and single phase. Two kinds of britholites were prepared for $0 \leq x \leq 1$: $Ca_9Nd_{1-x}An(IV)_x(PO_4)_{5-x}(SiO_4)_{1+x}F_2$ and $Ca_9Nd_{1-x}Th_x(PO_4)_5(SiO_4)_1F_{2-x}O_x$. We showed that the coupled substitution (Nd^{3+}, PO_4^{3-})<=>(Th^{4+}, SiO_4^{4-}) led to homogeneous and single phase compounds for all the compositions considered (up to 20 Wt.%). On the contrary, when performing the substitution (Nd^{3+}, F^-)<=>(Th^{4+}, O^{2-}), good incorporation rates were only obtained for $x \leq 0.5$ (i.e. 10 Wt.%). All the XRD patterns of the powders were recorded then the unit cell parameters were refined. The unit cell volume increased linearly versus x. For U(IV), the incorporation was incomplete: only 5-8 Wt.% of uranium was incorporated instead of 10 Wt.% required. XRD, EPMA and X-EDS experiments showed the simultaneous presence of calcium uranate (CaU_2O_5 or CaU_2O_6) in the solid. The incorporation of Pu(IV) was studied using Ce(IV) as a surrogate (r_{Pu}^{4+}=0.91 Å and r_{Ce}^{4+}=0.92 Å in 7-fold coordination). The results were quite good: major part of cerium was introduced in the structure but was partly reduced in Ce(III) during the heating treatment. The elaboration of sintered pellets of Th-britholite and Ce-britholite was performed. From dilatometry study, dense single phase pellets were prepared using uniaxial pressing then heating at 1400°C. Their chemical durability was studied during leaching tests using batch experiments in several media or considering dynamic conditions such as Soxlhet. We compared the dissolution of Th-britholite to Nd-britholite and to other phosphate ceramics. Finally, several neoformed phases, precipitated at the saturation of the leachate, were also identified.

11:30 AM DD3.9
f-Element Influence on the Size of Nanophase Phosphate Inclusions in Silica. James Beitz[1], S Skanthakumar[1], S Seifert[2] and P. Thiyagarajan[3]; [1]Chemistry Division, Argonne National Laboratory, Argonne, IL, Illinois; [2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, Illinois; [3]Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL, Illinois.

Our small angle neutron scattering, conventional x-ray diffraction, and laser-induced fluorescence studies, together with our conventional and anomalous small angle x-ray scattering work, have shown that heavy metal phosphate nanophases form when porous silica containing a surface coating of metal phosphate is heated above the pore collapse temperature. In our investigations of the factors that influence the formation and growth of such lanthanide and actinide phosphate phases in silica, we have observed an unexpected dependence of the size of the produced nanophases on the atomic weight of the chemical element. Studies designed to test our working hypothesis as to the underlying cause of this phenomenon, namely that pore coalescence competes with pore collapse, will be described. Work performed under the auspices of the Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under contract W-31-109-ENG-108.

11:45 AM DD3.10
Soft X-ray Synchrotron Radiation Investigations of Actinide Materials Systems Utilizing Near-edge X-ray Absorption Fine Structure and X-ray Emission Spectroscopy. David Shuh[1], S. M. Butorin[2], J. H. Guo[1], J. D. Denlinger[2], K. Kvashnina[2], I. L. Soroka[2], J. Nordgren[2], L. Werme[3], K. Ollia[4] and K. E. Roberts[5]; [1]LBNL, Berkeley, California; [2]Uppsala University, Uppsala, Sweden; [3]SKB, Stockholm, Sweden; [4]VTT Chemical Technology, VTT, Finland; [5]LLNL, Livermore, California.

Synchrotron radiation (SR) methods have been utilized with increasing frequency over the past several years to study scientific issues in actinide science, ranging from those of a fundamental nature to those that address a specifically-targeted technical need. In particular, the emergence of microspectroscopic and fluorescence-based techniques have permitted investigations of actinide materials at sources of soft x-ray SR. Spectroscopic techniques with fluorescence-based detection are useful for actinide investigations since they are sensitive to small amounts of material and the information sampling depth may be varied. These characteristics simplify both sample preparation and safety. The results from several soft x-ray SR x-ray emission spectroscopy (XES) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy investigations of actinide and actinide-relevant materials systems conducted at the Advanced Light Source will be discussed. In particular, the results from resonant inelastic soft x-ray scattering measurements are shown to be sensitive to the electronic structure and the chemical state of actinides. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL under Contract No. DE-AC03-76SF00098.

SESSION DD4: Actinide Solution and Interfacial Chemistry
Chair: David Shuh
Tuesday Afternoon, December 2, 2003
Gardner (Sheraton)

1:30 PM *DD4.1
Actinide Materials Research Supported By The Office Of Basic Energy Sciences, U.S. Department Of Energy. Lester R. Morss, SC-14, U.S. Dept. of Energy, Germantown, Maryland.

The Office of Science and its predecessor offices have supported research to define the scientific principles behind the physical and chemical behavior of actinide elements and their compounds. DOE supports studies that develop fundamental understanding of structure, electronic properties, bonding, and reactivity of the actinides. Areas of research include synthesis of actinide-containing materials; gas-phase and solid-state chemical bonding; measurements of chemical, thermodynamic, and magnetic properties; coordination and environmental chemistry; radiation damage studies; and theoretical methods to predict electronic properties, molecular structure, and reactivity. Research results have repeatedly confirmed that the actinides are a $5f$ element series under the $4f$ series in the periodic table. Structural systematics of the actinide metals, oxides, and halides as a function of atomic number are well established. Magnetic measurements have shown that the light actinide metals have delocalized $5f$ orbitals (*i.e.*, the $5f$ electrons form bands), whereas the f electrons become localized at americium. Thus, the magnetic behavior of the first part of the actinide series resembles that of the d transition metals but the heavier actinides exhibit behavior similar to the rare earth metals. Spectroscopic results have established electronic energy levels, crystal field splitting, and near-neighbor coordination. The role of the $5f$ electrons in bond formation remains the fundamental unanswered question in actinide chemistry, and provides the central focus for this program. The $5f$ orbitals participate in the band structure of materials that contain the light actinide metals and some of their alloys, and perhaps in molecular compounds. Molecular-level information on the geometry and bonding in solids, at surfaces, and in clusters can now be obtained at BES-supported facilities. This presentation will focus on recent achievements in actinide materials science research and potential opportunities that may result from nuclear energy initiatives and recent BES workshops.

2:00 PM *DD4.2
Actinide Chemistry on Geological and Biological Model Interfaces. Heino Nitsche, Department of Chemistry and Nuclear Science Division, University of California Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California.

Actinides can undergo a variety of complex chemical reactions in the environment. In addition to the formation of solid precipitates, colloids and dissolved solution species common to aqueous systems, actinide ions can interact with the surrounding geo and biomedia to change oxidation states or sorb on surfaces and colloids. Four important processes that can control the amounts and forms of the actinides in solution are: (1) precipitation, (2) complexation, (3) sorption and (4) colloid formation. These processes are not independent of one another and must be considered simultaneously. Sorption of aqueous actinide species on biological and geological matrices can be quantitatively described by a surface complexation or site-binding model. The disadvantage of this model is the difficulty in the experimental determination of the model parameters and surface reaction constants. Usually, a set of surface reactions and species are proposed based on knowledge of the solution speciation of the solute, and the reaction constants are usually derived by fitting computer-calculated absorption curves to experimental data. Because this process typically involves a large number of potentially adjustable parameters, it is likely to lead to non-unique parameter fitting and does not always lead to consistent sets of parameters for the same systems. Microbes in soil, sediment, and water can have a significant influence on the actinide source term. They exhibit the highest bio-diversity of any living organism and sometimes can adapt quickly to changing living conditions. Compared to processes involving

inorganic constituents, relatively little is known about bacterial interaction with actinides. A fundamental molecular-level understanding of sorption processes of actinides on environmental surfaces is required to better understand and predict their transport behavior in nature. Recently, several different surface-sensitive spectroscopic techniques have been applied to the characterization of the adsorbed species and surface reactions and a direct determination of the sorbed species and surface reactions has become available. Based on synchrotron X-ray absorption spectroscopy (XANES and EXAFS) measurements and time-resolved laser-induced fluorescence spectroscopy (TRLFS) studies on the homologous uranium system, molecular-level mechanistic details of the neptunium and plutonium interaction with common soil bacteria and manganese and iron oxide/oxyhydroxides will be presented. Areas will be outlined where integrated interdisciplinary research is needed to provide a more comprehensive understanding of these processes. Supported by the Natural and Accelerated Bioremediation Research Program (NABIR), Office of Biological and Environmental Research (OBER) and the Environmental Science Management Program (EMSP) of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

2:30 PM DD4.3

Np Speciation in Complex Systems. Lynda Soderholm[1], S. Skanthakumar[1], Peter C. Burns[2] and Jeremy Fein[2]; [1]Argonne National Laboratory, Argonne, Illinois; [2]Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana.

The speciation of actinide ions, even in simple systems, can be very difficult to determine for a variety of reasons, including their rich redox chemistry, their widely variable coordination geometries and the technical difficulties of handling small, radioactive samples. Unfortunately, much of the current interest in obtaining detailed metrical information about transuranic speciation involves complex systems that are of interest from either a nuclear waste management or an environmental contamination perspective. Np is a classic example. It has complex and interesting chemistry that has not been extensively explored. Depending on conditions, it can be found in the 3, 4, 5, 6 or 7 oxidation state. The most stable oxidation state in non-complexing aqueous media is the pentavalent state, where it exists in the linear dioxo cation as the [O=Np=O]+ moeity. The standard reduction potential of Np(V) is +0.567 V vs.SHE, and is therefore is very similar to that of trivalent Fe, which is +0.771 V. However, this standard reduction potential can be significantly influenced by coordinating ions and other competing factors. We report evidence that Np(V) is more easily reduced in a variety of solution and solid samples than expected from a review of the known chemistry. This increased ease of Np(V) reduction to the tetravalent state has important implications. Np(V) is very soluble in aqueous solutions whereas Np(IV) is generally considered insoluble when modeling environmental transport. In the solid phase, the little crystal chemistry that is known suggests that Np(V) and Np(IV) have very different coordination requirements. Our results will be put in context with this known chemistry. This work is supported by the NSF through the EMSI Center, at the University of Notre Dame, under contract EAR02-21966 and, together with the Actinide Facility, through the U.S. DOE, Basic Energy Sciences-Chemical Sciences, Office of Science, under contract No. W-31-109-ENG-38.

2:45 PM DD4.4

High Valence States of Plutonium and Neptunium in Alkaline Solution. Steven D. Conradson[1], David L. Clark[2], Pamela Gordon[2], W. Daniel Keogh[2] and C. Drew Tait[2]; [1]Materials Science and Technology Division, Los Alamos National Laboratorz, Los Alamos, New Mexico; [2]Materials Science and Technology Division, Los Alamos National Laboratorz, Los Alamos.

One of the more intriguing current issues in actinide chemistry is the speciation of the (VII) valence state in those elements that support it because of the relationship between the electronic structure and the geometry of their coordination complexes. Np and Pu (VII) are stabilized in highly alkaline solutions, allowing this issue to be elucidated. In addition to other spectroscopies, XAFS measurements provide incisive structural information on these compounds. Although neptunium occurs as the hypothesized tetraoxo complex in the homogeneous hydroxide species, the bis-oxo is a competing ground state that can evidently be produced by, e.g., the addition of a bidentate ligand such as carbonate to form the mixed hydroxo-monocarbonato complex. This bistable situation rectifies itself for Pu(VII), where identical conditions produce only the bis-oxo compound. Minimal changes in the Pu-O distances and numbers of atoms are consistent with a small shift in the absorption edge energy that suggests that the actual charge (and electron configuration on the Pu ion is only slightly affected by the increase in formal valence. Electronic structure considerations show how this situation occurs.

3:30 PM *DD4.5

***InSitu* Actinide X-ray Absorption Spectroelectrochemistry.** Mark R Antonio and L Soderholm; Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

As a solvent and coordinating ligand, water provides the benchmark system upon which to construct a comprehensive picture of the redox speciation−coordination as a function of oxidation−of the actinide elements. Toward this end, compilations of standard electrode potentials, such as those found in potential-pH (Pourbaix) diagrams, are heavily used to assess the complex equilibrium behavior of the uranium and the *trans*-U aquo ions. Yet, Pourbaix diagrams do not provide metrical information and, moreover, typically provide little information about ligands other than H_2O, OH^-, and O^{2-}. Through use of purpose-built equipment and new methodology, results from *insitu* spectroelectrochemical experiments are advancing the understanding of 5f-ion redox speciation in solutions. By using electrochemical techniques in simultaneous combination with X-ray absorption spectroscopy, we can stabilize a targeted charge state of a solution complex, and probe the coordination of selected ions. In addition, we can acquire sufficient XANES over a range of controlled electrochemical potentials, in the vicinity of a redox couple, to perform a Nernst analysis. To demonstrate this approach, we have examined the coordination chemistry of actinide ions as a function of redox state in complexes in different solvents and with different ligands, including small, electrochemically-inactive ones like water and large, electroactive ones like polyoxometalate clusters. The latter ions can obscure the optical and electrochemical response of the 5f-ion itself. In this situation, the *insitu* XANES approach provides information about formal electrode potentials that is not obtainable from conventional spectrophotometric measurements, cyclic voltammetry, or potentiometric titrations alone. Our methods and equipment will be discussed in light of the results and their implications to studies of other systems of fundamental and practical interest in which electrons are involved. This work is supported by the U.S. DOE, Basic Energy Sciences−Chemical Sciences, Office of Science, under contract No. W-31-109-ENG-38.

4:00 PM DD4.6

On the Physical Nature of Uranyl Charge Transfer Vibronic Interactions. Guokui Liu and Xueyuan Chen; Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

We address the electronic properties of uranyl ions in solids and solutions with an emphasis in theoretical understanding of charge transfer vibronic transitions and uranyl luminescence dynamics. A general theory of ion-phonon interaction has been modified for modeling and simulating multi-phonon vibronic spectra and fluorescence lifetimes. Spectroscopic data for uranyl ions in crystals, glasses, and solutions have been analyzed to achieve a predictive understanding of the uranyl-ligand vibronic interactions. By adjusting the Huang-Rhys ion-phonon interaction parameters, an excellent agreement between theory and experiment has been accomplished for uranyl ions in a variety of ligand environments. Although, optical spectroscopy and laser-induced fluorescence are widely used in actinide chemistry and speciation, the nature of photochemistry and photophysics of uranyl complexes is currently lacking a fundamental understanding in general. Our modeling and simulation provide insights into the physical nature of uranyl vibronic interaction and its influence on optical spectroscopic properties, thus provide a useful framework as well for characterizing photochemical properties of uranyl in complexes.

4:15 PM DD4.7

Hierarchical Structures of Aqueous Pu Colloids using Synchrotron Techniques. S Skanthakumar[1], L Soderholm[1] and P Thiyagarajan[2]; [1]Chemistry Division, Argonne National Laboratory, Argonne, Illinois; [2]IPNS Division, Argonne National Laboratory, Argonne, Illinois.

Tetravalent Pu ions in slightly acidic aqueous solutions are known to aggregate. Earlier x-ray and electron diffraction experiments, which were performed mostly on dried samples, showed broad Bragg peaks that were thought to be due to the amorphous nature of these aggregates. Our conventional x-ray diffraction studies showed significant differences between solution and dried samples and hence it was decided that experiments targeted on the structural properties within the aggregates must be conducted on solution samples. We have probed aqueous solutions containing tetravalent Pu aggregates at different length scales using x-ray absorption spectroscopy (<4 $\AA$), high energy x-ray scattering (<20 $\AA$) and small angle x-ray scattering ($\sim$ 5 - 1000 $\AA$) techniques. Both X-ray absorption (XAS) and high energy x-ray scattering (HEXS) data clearly indicate that the local structure about Pu is similar to that of Pu dioxide. The difference between the data of Pu colloids and crystalline PuO_2 can be accounted for by the small size of Pu aggregates. We conclude that it is the small size of the particles and not the disorder within the

particle itself, that is responsible for the broadened peaks observed in the scattering data. Pair distribution functions obtained from the Fourier transformation of the HEXS data show correlations up to 15 $\AA$. Refinement of the HEXS data using PuO_2 type Fm3m structure with a limited size gave a radius of 8.6 $\AA$ for these colloids. Small angle x-ray scattering data show that the Pu aggregates have a fractal type of structure with a mass fractal dimension of 2.3 and a fundamental particle size of $\sim$8.6 $\AA$. We conclude from these results that the fundamental PuO_2 particles aggregate to form clusters whose sizes are larger than 150 $\AA$. This work is supported by the U.S. DOE, Basic Energy Sciences,Chemical Sciences and Material sciences, Office of Science, under contract No. W-31-109-ENG-38.

SESSION DD5: Poster Session: Actinide Science and Technology Poster Session
Chair: Jim Tobin
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

DD5.1
Electronic structure of UAsSe and USb2 compounds: the 5f photoemission. Elzbieta Guziewicz[1], Tomasz Durakiewicz[1], Martin T Butterfield[1], Clifford G Olson[2], John J Joyce[1], Al J Arko[1], John L Sarrao[1], Andrzej Wojakowski[3], Tomasz Cichorek[3,4] and Joe D Thompson[1]; [1]MST-10, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Ames Laboratory, Ames, Iowa; [3]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland; [4]Max Planck Institute for Chemical Physics of Solids, Dresden, Germany.

UAsSe and USb2 exhibit many interesting properties, these include magneto-transport phenomena, which are characteristic of uranium compounds, as an enhanced specific-heat coefficient and magnetic ordering at low temperature. It is well established that the unusual properties of uranium compounds are closely related to the correlation between the U5f electrons and their hybridization with the conduction band. Single crystals of UAsSe and USb2 were studied at 15K by angle-resolved photoemission in the photon energy range between 20 eV and 110 eV. The overall energy resolution for the lowest energy range was 24 meV, and the momentum resolution was 0.09A-1. The photon energy and momentum resolution allow observation of dispersive photoemission features within 100 meV of the Fermi level (EF). Both uranium systems exhibit similar electronic properties, most notably a very narrow and dispersive photoemission peak situated in the vicinity of EF. From cross-sectional arguments it is postulated that this structure has mixed conduction electron/U 5f character. Resonant photoemission studies also give evidence of the U5f-conduction band hybridization. The natural linewidth of the near EF feature of USb2 was found to be less than 10 meV. The dispersion of this peak along the gamma to X direction of the Brillouin zone is 14 meV. The 5f feature in UAsSe is slightly broader than that in USb2. It is situated about 12 meV closer to the Fermi edge, and exhibits a 50 meV dispersion in the normal emission spectra. A 10 meV dispersion is also visible in the normal emission spectra of USb2, which is evidence that the electronic structures of both USb2 and UAsSe have some 3D component although the in-plane coupling is strongest. The photoemission investigations of UAsSe and USb2 showing narrow band behavior of 5f electrons provides new insight into band magnetism in uranium compounds. This work was supported by the U.S. Department of Energy, Office of Science, Division of Material Science and Engineering

DD5.2
Comprehensive Decontamination Method Data Base. Evgueni Pavlovich Emets and Pavel Petrovich Poluectov; VNIINM, Moscow, Russian Federation.

The DB is a versatile decision support information system. It permits making the best choice of decontamination technologies, procedure and agents. It is meant for educated and skilled experts in radiochemistry and for specialists in physics, chemistry, physical chemestry and other fields. The DB data must meet typical demands of users specialising in decontamination. The unit record contains information on the surface material, contamination, decontamination effectiveness, corrosion impacts and references.The data presentation makes possible the realization of a record selection algorithm for "lay" user to support the decontamination decision approaching the best one. The full-scale DMDB will include the following features -liquid decontamination technologies for metal surface, -non-chemical decontamination techniques, -high-temperature water-free methods, decontamination of soils, buildings, hydrogeological structure, -facilities and methods for decontamination, ets.

DD5.3
A New Paradigm for the Determination of the 5f Electronic Structure of Pu and the Actinides. James Tobin, CMS, LLNL, Livermore, California.

Despite recent intensive experimental effort [1-3], the electronic structure of Pu, particularly d-Pu, remains ill defined. An evaluation of our previous synchrotron-radiation-based investigation of a-Pu and d-Pu [1] has lead to a new paradigm for the interpretation of photoemission spectra of U, Np, a-Pu, and d-Pu . This approach is founded upon a model in which spin and spin-orbit splittings are included in the picture of the 5f states [4] and upon the observation of chiral/spin-dependent effects in non-magnetic systems. [5,6] By extending a quantitative model developed for the interpretation of core level spectroscopy in magnetic systems [7], it is possible to predict the contributions of the individual component states within the 5-f manifold. This has lead to a remarkable agreement between the results of the model and the previously collected spectra of U, Np, and Pu , particularly d-Pu, [1-3,8] and to a prediction of what we might expect to see in future spin-resolving experiments. [9] This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. *Collaborators: B.W. Chung, LLNL; R.K. Schulze, LANL; D.K. Shuh, LBNL 1. J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, D.K. Shuh, G. van der Laan, D.A. Arena, and J.G. Tobin, Surface Science Letters 499, L141 (2002). 2. T. Gouder, L. Havela, F. Wastin, and J. Rebizant, Europhys. Lett. 55, 705 (2001); MRS Bulletin 26, 684 (2001); Phys. Rev. Lett. 84, 3378 (2000). 3. A.J. Arko, J.J. Joyce, L. Morales, J. Wills, J. Lashley, F. Wastin, and J. Rebizant, Phys. Rev. B 62, 1773 (2000). 4. S.Y. Savrosov and G. Kotliar, Phys. Rev. Lett. 84, 3670 (2000). 5. Ch. Roth et al, Phys. Rev. Lett. 73, 1963 (1994). 6. K. Starke et al, Phys. Rev. B 53, 10544 (1996). 7. J.G. Tobin and F.O. Schumann, Surface Science 478, 211 (2001). 8. J.R. Naegele, Photoem. of Solids, Landolt-Bornstein III/B,183 (1994). 9. J. Tobin, D.A. Arena, B. Chung, P. Roussel, J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, and D.K. Shuh, Photoelectron Spectroscopy of Plutonium at the Advanced Light Source, J. Nucl. Sci. Tech. Supplement 3, 98 (2002).

DD5.4
Role of Spin-Orbital Splitting of 5f-Orbitals of Uranium Atom in the Formation of Its Chemical State. Yuri F. Batrakov, Andrey G. Krivitsky and Elena V. Puchkova; Section of Radiochemistry, Faculty of Chemistry, St. Petersburg State University, St. Petersburg, Russian Federation.

This paper deals with one of fundamental problems of chemistry: the influence of relativistic effects (RE) on the chemical properties of atoms of heavy elements. The aim of this work is to detect experimentally RE in the oxide series of uranium compounds, to describe them quantitatively and to determine their role in chemical state formation of a heavy atom. Experimental basis is the chemical shift (ChSh) method of hard x-ray lines. The main task is the choice and the study of parameters derived from ChSh and reflecting the influence of spin-orbital interaction (SOI) between 6d- and 5f-valent electrons on the uranium state and the interpretation of data based on the atomic Dirac-Hartree-Fock calculation in the framework of isolated atom model. ChSh values were measured for 15 uranium L-lines in oxides with the composition of UO_{2+x} (x=0$\div$1) and in UF_4 with respect to $UO_{2.00}$. According to the data of ChSh of spin-doublet lines, differences in energies of spin-orbital splitting (SOS) $\Delta\delta$nl$\pm$ of internal 2p-, 3d-, 3p-, 4d- and 4p-levels of uranium atom were calculated. They demonstrate linear dependence on the x coefficient at oxygen. It was shown that the origin of the $\Delta\delta$nl$\pm$ value is due to the redistribution of $5f_+ \leftrightarrow 5f_-$ electron and spin density (Q5f$\pm$) between $5f_\pm$-levels of the fine structure, which does not change the charge on the uranium atom. This can explain the fact that $\Delta\delta$nl$\pm$ for UF_4 is smaller by one order of magnitude than for uranium oxides. The values of Q6d$\pm$ are negligible in both cases. The exclusion of SOI of outer-shell electrons (by the transformation of ChSh of individual lines into ChSh of multiplets) made it possible to calculate partial charges on uranium atoms in terms of changes in population of 5f- and 6d-uranium orbitals. The limiting value of Q5f$\pm$ equal to (1.5$\pm$0.1)e was calculated on the basis of the established relationship between $\Delta\delta$nl$\pm$ and ChSh of multiplets. A possibility of determining the true valence value was considered on the basis of quantitative evaluations of Q5f$\pm$ and the difference in populations of 5f- and 6d-orbitals. It is also suggested that the interatomic relativistic $5f_+ \leftrightarrow 5f_-$ transition is a "fine energetic turning" to a specific chemical state. It is because of this transition that unique chemical properties of uranium in the "uranium - oxygen" system are formed: polyvalence of the oxide series, numerous structural modifications, and a structural chemical compromise, i.e. the maintenance of oxide structure with increasing oxygen content ($UO_{2.00} \rightarrow UO_{2.25}$). On the basis of these results, the main conclusion was drawn: it is necessary to take into account the relativistic effect of SOS of 5f-levels in the study of chemical (valent,

charge, and magnetic) state of the uranium atom. This work was carried out with the financial support of the Ministry of Education of the Russian Federation - grant # PD 02-1.3-306.

DD5.5
The Properties of Actinide Nanostructures. Thomas Trelenberg, Stephen Glade, Jim Tobin, Phil Sterne and Alex Hamza; Lawrence Livermore National Lab, Livermore, California.

Predicting the aging behaviors of actinide materials is a problem requiring advances in both theoretical understanding and experimental observation. This work seeks to determine the various correlation and spin contributions to the electronic structure active in actinide elements through observations of structural and electronic evolution in these materials as a function of particle size. Results from these experiments will be used to confirm the several proposed theoretical descriptions of these materials. The measurements [which will include x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunnel microscopy (STM)] will be carried out on a number of different uranium and plutonium systems, such as single crystalline nanoparticles and 1-D wires, produced via pulsed laser deposition (PLD). This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

DD5.6
Inverse Photoemission Spectroscopic studies of Plutonium. Paul Roussel, Peter Morrall, Simon J Tull and David A Geeson; AWE, Berkshire, United Kingdom.

The position of plutonium in the actinide series marks the transition from itinerant to localised or atomic like 5f electrons. The 5f electrons of plutonium become more localised when the metal is heated, changing through its six temperature induced allertropic phases. Photoelectron spectroscopy has displayed itself as a useful technique to investigate the nature of the 5f electrons in plutonium metal, alloys and compounds. The majority of data has been acquired using laboratory photon sources,(1) however, the first synchrotron photoemission study of plutonium was recently reported.(2) The photoemission techniques focus on the occupied states, which for the plutonium 5f are nearly half full. It would be desirable to measure the unoccupied states aswell to obtain a better understanding of the 5f states. Baer et al. have reported the combined use of monochomatic X-ray photoelectron and bremsstrahlung isochromat spectroscopies to acquire information on both the occupied and unoccupied states of thorium and uranium.(3) To the best of our knowledge there are no reports of the unoccupied states of metal/compounds containing plutonium. We have set out to acquire such data. Details of our equipment and the first inverse photoemission spectra of plutonium will be presented. (1)For example see: J. R. Naegele et al., Structure and Bonding 59/60 (1985) 199. (2) J. Terry et al., Surf. Sci., 499 (2002) L141. (3) Y. Baer et al., Phys. Rev., B21 (1980) 2060.

DD5.7
Fine structural characterization of actinides under high pressure by X-ray powder diffraction in laboratory: first results on a PuGa alloy. Philippe Faure[1] and Pascal Pochet[2]; [1]CEA, Is Sur Tille, 21120, France; [2]CEA, Monts, 37260, France.

The prediction of the physical properties of actinides and their alloys under non-ambient conditions (pressure or temperature) or during aging (changes in chemical composition and creation of structural defects due to self-irradiation) remains a challenge today. The determination and understanding of the electronic structure of these materials is an essential step. As the organization of atoms is linked to the electronic structure, the fine structural characterization of these materials under pressure gives precious information that could be compared to the prediction of theoritical models. Today, angular-dispersive x-ray diffraction experiments performed at synchrotron sources give high-quality structural data even for pressures of one megabar. But access to such instruments for experiments on radioactive materials remains restricted. A new laboratory x-ray powder diffractometer (a Mo rotating anode) has been built and optimized to allow the acquisition of high-quality data on actinides under high static pressures. An imaging plate detector is mounted on the diffractometer, a goniometer allows high precision positioning of the diamond anvil cell (DAC) and pressure is measured without moving the DAC by measuring the fluorescence of gauges such as rubis or borates. The DACs used have a wide angular apperture (40° in 2θ) and are equiped with a membrane for fine tuning of the pressure. The pressure transmitting media used (Ar or He) ensure good hydrostatic conditions. The quality of the diffraction data obtained with such a device allows structural refinements with the Rietveld method. The equation of state of a Pu-8at%Ga alloy in the δ phase (fcc structure) has been determined with a good accuracy. The first derivative of the isothermal bulk modulus with pressure is found to be anormally low. This value could be the consequence of the evolution of the electronic structure of the material under pressure (delocalization of 5f electrons). Moreover, the effects of pressure on the equation of state of an aged alloy have been measured.

DD5.8
Confocal Micro X-Ray Fluorescence Instrument For Radioactive Materials Characterization. George J Havrilla[1] and Ning Gao[2]; [1]Chemistry, Los Alamos National Lab, Los Alamos, New Mexico; [2]X-Ray Optical Systems, East Greenbush, New York.

A novel instrument has been designed and built using monolithic polycapillary optics on both the excitation and detection sides of the instrument. This allows the overlap of both focal spots, one from the excitation beam of the X-ray tube and the focal spot of the detection polycapillary, which collects the emitted X-rays from the specimen. The primary objective of this confocal instrument is to excite and detect elements within radioactive specimens. The radiation background in radioactive specimens usually swamps the analytical signal in an energy dispersive detector. This prohibits the use of energy dispersive X-ray fluorescence instruments from characterizing radioactive specimens. Previous work has shown that the use of a polycapillary in front of the detector effectively screens the radiation from the detector. The use of a polycapillary optic on the detector side of the instrument allows the use of an EDS detector for radioactive specimens. In addition to removing the radiation background the added optic on the detector side reduces normal background scatter into the detector due to the spatial overlap of the two focal spots for the excitation and detection optics. This results in a small increase in signal to noise for non-radioactive specimens. Another benefit of the spatial overlap of the two focal spots is a small increase in spatial resolution. Design considerations, optic performance parameters and preliminary testing on model analytes will be presented. Characterization of uranium-based materials will illustrate the analytical capabilities on radioactive samples.

DD5.9
Structural properties of non-Fermi liquid $CeRhRuSi_2$. S.-W. Han[1], C. H. Booth[1], J. L. Sarrao[2] and J. D. Thompson[2]; [1]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Los Alamos National Laboratory, Los Alamos, New Mexico.

The structural properties of the non-Fermi liquid (NFL) system $CeRhRuSi_2$ were studied with temperature dependent x-ray absorption fine structure (XAFS) and x-ray diffraction measurements. The XAFS data analysis at Ce L_3 -, Rh K- and Ru K-edges shows that the crystalline structure of $CeRhRuSi_2$ is well-ordered and that the intrinsic bond length disorder at all atomic sites is negligibly small, in spite of the random occupation of Rh/Ru sites. Pair-distribution function (PDF) analysis of x-ray diffraction data corroborate these results. These data imply that the NFL behavior in $CeRhRuSi_2$ cannot be explained with a Kondo lattice disorder model alone. In addition, we do not observe any annealing effects. We will present these results and discuss the spin-spin interactions in this system.

DD5.10
The Spatial Distribution of Native Impurities in Uranium: Their Effect, and the Effect of Implanted Impurities, on Gas-Surface Reactions. Wigbert J. Siekhaus, Kuang Jen J. Wu, Thomas Felter and William McLean; Dept of Materials Science and Chemistry, Lawrence Livermore National Laboratory, Livermore, California.

Uranium contains typically impurities at the level of .1 and 1 weight part per thousand, ranging from hydrogen to tungsten. These impurities affect the chemical reactivity of the surface as well as the bulk properties of the material. To determine the spatial distribution of these impurities and their chemical moiety we fracture uranium samples under UHV conditions in a pre-treatment chamber, transfer the sample under UHV conditions into a secondary ion mass spectrometer and determine impurity distribution and composition with high resolution ($\leq$ 100nm). The sample is thereafter transferred back into the pretreatment chamber, exposed to gases (e.g. air, water vapor, oxygen, nitrogen, hydrogen) and re-analyzed to determine the effect of impurities on the initial local reactivity at the impurity sites. This reaction-analysis technique is limited to thin surface reaction layers. After prolonged exposure to air an oxide layer incorporating the native impurities is formed. This oxide layer is generally protective, but prolonged exposure to hydrogen causes highly localized uranium hydride formation in the underlying uranium resulting in fracture of the oxide layer. To determine whether the localization of the attack is due to variation in uranium oxide thickness or to local incorporation of impurities into the oxide layer, a scanning Raman spectrometer is used to generate with $\sim \leq 10\mu$m

resolution a x-y map of its composition and thickness. After exposure to hydrogen the x-y coordinate of the attack-site is correlated with the composition-thickness map. Equilibrium chemistry predicts that uranium carbide will not react with air or hydrogen. To test and quantify this in practice, uranium has been implanted with the equivalent of 200 mono-layers of carbon, exposed to air for an extended period, and the thickness of the reaction layer monitored by atomic force microscopy. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

SESSION DD6: Theory of Actinides: Elemental Phases, Alloys and Compounds
Chair: Bill Wolfer
Wednesday Morning, December 3, 2003
Gardner (Sheraton)

8:30 AM *DD6.1
Thermodynamic Properties Of Light Actinide Compounds And Alloys From Den-sity Functional Theory. P. A. Korzhavyi[1], L. Vitos[1,2], D. A. Andersson[1] and Borje Johansson[1,3]; [1]Dept of Materials Science and Engineerng, Royal Institute of Technology (KTH), Stockholm, Sweden; [2]Research Institute for Solid State Physics and Optics, Budapest, Hungary; [3]Department of Physics, Uppsala University, Uppsala, Sweden.

A theoretical approach has been developed that allows one to obtain thermody-namic properties of actinide-based alloys and compounds from first-principles electronic structure calculations based on density functional theory.[1] The calcula-tions reported here have been performed within the Korringa-Kohn-Rostoker Green's function (KKR-GF) method[2] and made use of the recently developed Local Airy Gas (LAG) approximation[3] for the exchange-correlation po-tential. This approach works well for pure U and Pu metals in their low-temperature crystal structures and, in conjunction with the disordered local moment (DLM) model of the magnetic structure, is capable of reproducing the basic thermodynamic properties (such as lattice parameter and bulk modulus) of δ-Pu and Pu-Ga alloys. We use the same approach to calculate the enthalpies of formation and equilibrium lattice constants for selected stoichiometric and non-stoichiometric compounds in the Pu-O-H and U-O-H ternary systems. Point defects in non-stoichiometric solid solutions $UO_{2\pm\delta}$ and $PuO_{2\pm\delta}$ have been studied by means of the lo-cally self-consistent Green's function (LSGF) method[4]. Supercells with various kinds of native point defects, and also with hydrogen impurities, in UO_2 and PuO_2 have been considered in order to analyze the constitution and stability of non-stoichiometric phases. We find, in accordance with Pu-O phase diagrams,[5] that sub-stoichiometric $PuO_{2-\delta}$ alloys contain oxygen vacancies as constitutional defects in the interval between Pu_2O_3 (C-type) and stoichiometric PuO_2. Interstital oxygen atoms are identified as constitutional defects in hyperstoichiometric $PuO_{2+\delta}$, which is calculated to be slightly unstable relative to PuO_2 and O_2. The reaction of PuO_2 with water to form $PuO_{2+\delta}$ is also found to be endothermic, whereas the reactions with stronger oxidants such as atomic oxygen or H_2O_2 are exothermic. This work was supported by SKB AB, The Swedish Nuclear Fuel and Waste Management Company. 1. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965). 2. A. V. Ruban and H. L. Skriver, Comp. Mat. Sci. **15**, 119 (1999); L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett.**87**, 156401 (2001). 3. L. Vitos, B. Johansson, J. Kollár, and H. L. Skriver, Phys. Rev. B **62**, 10046 (2000). 4. A. Abrikosov *etal*., Phys. Rev. B **56**, 9319 (1997). 5. R. G. Haire and J. M. Haschke, MRS Bulletin **26**, 689 (2001).

9:15 AM DD6.2
Electronic structure calculations of Pu. Per Soderlind, LLNL, Livermore, California.

Density-functional (DF) electronic-structure calculations for α, β,γ, and δ Pu have been carried out using a full potential linear muffin-tin orbitals (FPLMTO) method. The theory include magnetic interactions such as spin-orbit coupling, spin polarization, and orbital polarization within the general gradient approximation (GGA). The total energies are compared to a recently proposed pseudo α structure. The results suggest that all experimental phases are well described but that the pseudo structure has too high energy. Hence, a unified approach can be used for these phases of Pu and no need for semi-empirical parameters are needed. This is valuable because the theory is then capable of predicting other properties of interest, such as equation-of-state, elastic constants, phonons, defect properties, etc. It should be emphasized that spin polarization is necessary to correctly describe plutonium within the DF-GGA theory. This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

9:30 AM DD6.3
Fully-Relativistic Spin-Polarized Linear Combinations of Gaussian-Type-Orbitals Calculations For fcc Pu.
Jonathan Carl Boettger, Group X-7, Los Alamos National Laboratory, Los Alamos, New Mexico.

The magnetic ordering of fcc plutonium (Pu) has been investigated using the relativistic linear combinations of Gaussian type orbitals - fitting function (LCGTO-FF) method, within the generalized gradient approximation (GGA). Three types of collinear spin-orderings were considered; ferromagnetic with spins aligned in the (001) direction and two antiferromagnetic (001)-layer structures with spins aligned either perpendicular to each plane (001) or parallel to each plane (100). For each ordering, the total energy and spin-moment were calculated with and without spin-orbit coupling. In both cases, the ground state is predicted to be antiferromagnetic. Spin-orbit coupling acts to stabilize the (001) orientation relative to the (100) orientation. The antiferromagnetic (001) state is predicted to be lower in energy than the nonmagnetic state by roughly 40 mRy per atom at zero-pressure. The lattice constant obtained here for the antiferromagnetic (001) state (8.69 bohr) is in better agreement with the experimental lattice constant (8.80 bohr) than the predicted lattice constant for the nonmagnetic state (8.12 bohr). This work was supported by the U.S. Department of Energy under contract W-7405-ENG-36.

9:45 AM DD6.4
Chemical Short Range Order Effects on Stability in delta Pu-Ga alloys. Gregory Robert[3], Catherine Colinet[1], Bruno Siberchicot[3] and Alain Pasturel[2]; [1]INPG, Laboratoire de Thermodynamique et Physico-Chimie Metallurgique, Saint Martin d'Heres, France; [2]CNRS, Laboratoire de Physique et Modelisation des Milieux Condenses, Grenoble, France; [3]CEA, Departement de Physique Theorique et Appliquee, Bruyeres-le-Chatel, France.

The structural stability of Pu-Ga alloys is studied using a method based on the local spin-density approximation including non-local corrections to the exchange-correlation functional (generalized gradient approximation). First, both LAPW and PAW methods have been used to calculate the energies of formation of five intermediate phases which occur in the Ga-Pu phase diagram. Then PAW calculations have been performed for various superstructures based on the fcc lattice in order to get the interaction parameters necessary to describe the energetics of the δ Pu-Ga solid solution. The cluster variation method has been used to discuss the effects of the chemical short-range order on the stability of the delta Pu-Ga solid solution as a function of temperature. The solid part of the Pu-rich Pu-Ga phase diagram involving Pu phases, δ Pu-Ga solid solution, and Pu3Ga compound is calculated. The importance of the chemical short-range order on Ga solubility in δ-Pu is underlined.

10:30 AM DD6.5
Electronic Structure Calculations of δ-Pu Based Alloys.
Alexander I. Landa[1], Per Soderlind[1] and Andei Ruban[2]; [1]Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California; [2]Technical University of Denmark, Lyngby, Denmark.

It has been proposed that δ-Pu is stabilized at higher temperatures by magnetic interactions driving a disordered magnetic (DM) state. At lower temperatures, however, the magnetic moments are expected to align in an antiferromagnetic (AF) fashion which has been shown to destabilize δ-Pu mechanically. Consequently, δ-Pu is unstable below 593 K but can be stabilized at lower temperatures when alloyed with a small amount of a suitable δ-stabilizer. Here we explain this stabilizing effect in terms of the balance between ordered and disordered magnetism and how this balance is offset by the addition of an alloying component. For this purpose density functional electronic structure calculations for δ-Pu and δ-Pu based alloys have been carried out using the Korringa-Kohn-Rostocker method (KKR) within the Green's function formalism. The calculations show that an alloy component larger than δ-Pu (Ce, Am, Cm, Th, and Ac) has a stabilizing effect, whereas a magnetic alloy component that is smaller (Mn, Fe, and Co) has a strongly destabilizing effect on δ-Pu. Detailed calculations have been performed for $Pu_{1-x}Am_x$ (FCC) system which is stable experimentally at room temperature in a wide concentration range ($0.06 \leq x \leq 0.80$). Calculated density of Pu-Am alloys agrees well with experimental data and shows a positive deviation from Vegard's law. Effective cluster interactions obtained from the structure inverse method have been applied in Monte Carlo simulations which indicate a 'DM' $\rightarrow$ 'AF' phase transition for pure δ-Pu at $T_c \sim 550$ K. We also found that T_c decreases as Am concentration increases. The possibility of stabilization of AF phase in $Pu_{1-x}Am_x$ system is discussed. This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract

W-7405-Eng-48. Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

10:45 AM DD6.6
Phase Stability in the Pu-Ga System From First Principles and Molecular Dynamics Calculations. Marius Stan, Michael I Baskes and Krishna Muralidharan; Los Alamos National Laboratory, Los Alamos, New Mexico.

Plutonium is one of the most complex elements in the periodic table. Its zero pressure phase diagram contains seven condensed phases. The f-electrons in Pu seem to switch from bonded to non-bonded states in different crystal structures. Similarly, Gallium exhibits five solid equilibrium phases at various temperatures and pressures and is liquid above room temperature at normal pressure. The experimental Pu-Ga phase diagram shows numerous additional phases and is still the subject of debate, mostly in the low temperature, low Ga content area. The Modified Embedded Atom Method (MEAM) formalism has previously been applied to Pu and Ga. Using experimental data from the Ga-stabilized fcc δ-phase and the monoclinic α-phase, a MEAM potential for Pu has been developed. This potential has been applied to all of the Pu phases. Similarly density functional calculations using the Generalized Gradient Approximation (GGA) have been used to develop a MEAM potential for Ga. First principle calculations and experimental results have been used to obtain the parameters for the Pu-Ga system. By the means of thermodynamic switching and thermodynamic integration, the enthalpy resulted from the molecular dynamics calculations was employed to determine the free energy of Pu-Ga alloys inter-metallic compounds and solutions. Consequently, the chemical potentials of components in all phases have been calculated to determine the equilibrium points and lines in the phase diagram.

11:00 AM DD6.7
SIC-LSD study of actinide compounds. Leon Petit[1,2], Axel Svane[3], Walter M Temmerman[4] and Zdzislawa Szotek[4]; [1]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Institute of Physics and Astronomy, University of Aarhus, Aarhus, Denmark; [4]Computational Science and Engineering, Daresbury Laboratory, Daresbury, United Kingdom.

The electronic structure of actinide compounds is studied using first principles quantum mechanics, realized with the self-interaction-corrected (SIC) local spin density (LSD) approximation. This method allows for the description of actinide ions, with some f-electrons localized in atomic-like orbitals, while other f degrees of freedom are forming hybridized bands. The groundstate valency configuration of the actinide ion is deduced from total energy considerations.

11:15 AM DD6.8
Energies, volumes and the geometries of point defects in alpha and delta Pu. Babak Sadigh and Wilhelm G. Wolfer; Chemistry and Materials Science, Lawrence Livermore National Lab, Livermore, California.

We have calculated the formation energies and volumes of point defects, i.e. vacancies and interstitials, in alpha and delta phases of pure Pu, using the first-principles density-functional theory framework within the Generalized Gradient Approximation. We have performed full relaxation of the atomic coordinates and thus obtained the preferred local geometry of the point defect configurations in the two important phases of Pu. . In particular we discuss the specific topology of the point defects and their energetics in the alpha-Pu structure. The cohesive energy and the volume of the delta-phase can only be accurately predicted when spin polarization is employed. We discuss the effect of point defects on the surrounding magnetic configuration of the delta-phase. We discuss the implication of our calculations on the experimental observations of the aging of Pu.

11:30 AM DD6.9
Hybrid Density Functional Theory Studies of PuO2 and Pu2O3. J. A. Sordo[1], K. N. Kudin[1], G. E. Scuseria[1] and Richard L. Martin[2]; [1]Department of Chemistry, Rice University, Houston, Texas; [2]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Hybrid density functional theory (DFT) has recently been shown to significantly improve the description of the band gap, photoemission spectrum, magnetic properties and lattice constants of UO2 compared with conventional approaches such as the local density approximation (LDA) and generalized gradient approximation (GGA) [Kudin, Scuseria, and Martin, Phys. Rev. Lett. 89, 266402(2003)]. In the present contribution, we report on similar hybrid DFT calculations applied to PuO2 and Pu2O3. We find that hybrid DFT predicts these systems to be insulators, as opposed to the metallic behavior predicted by the LDA/GGA. We compare results for a number of properties among the various approximations, and with available experimental information. $\sim$

11:45 AM DD6.10
Magnetic State of UGe_2 under Pressure. Alexander B. Shick[1], Vaclav Janis[1], Vaclav Drchal[1] and Warren E. Pickett[2]; [1]Institute of Physics ASCR, Prague, Czech Republic; [2]University of California, Davis, California.

The possibility of coexistence of superconductivity and ferromagnetism has long been of theoretical interest. We focus here on the case of UGe_2, for which superconductivity occurs in the pressure range of 10-18 kBar, coexisting with robust ferromagnetism. The correlated band theory picture (LSDA+U) has been applied to UGe_2, and the full-potential linearized augmented plane-wave (FP-LAPW) method including spin-orbit coupling is used to calculate the total energy and the spin and orbital magnetic moments, and their dependence on pressure, for a normal state of UGe_2 at T=0. Over a range of volumes (*i.e.* pressures), two nearly degenerate ferromagnetic states are obtained, which differ most strikingly in their orbital moment (on uranium) character. The calculated moment, and its separation into spin and orbital parts, is consistent with one set of recent polarized neutron scattering data. These two states are strong candidates for the two ferromagnetic phases, one low-temperature - low-pressure, the other higher-temperature - higher pressure. Orbital (and spin) excitations built from fluctuations between these uranium configurations provide a possible novel mechanism of pairing in UGe_2.

SESSION DD7: Superconductivity, Correlated Behavior and Quantum Criticality
Chair: Malcolm Nicol
Wednesday Afternoon, December 3, 2003
Gardner (Sheraton)

1:30 PM *DD7.1
Plutonium Superconductivity: Implications for f-electron Localization. John L Sarrao, Los Alamos National Laboratory, Los Alamos, New Mexico.

We discuss the 18-K superconductivity observed in PuCoGa5 and argue that this superconductivity is unconventional. In this scenario, PuCoGa5 is the 5f analog of the family of heavy fermion superconductors CeMIn5 (M=Co,Rh,Ir). Further, we argue that the high Tc observed in PuCoGa5 derives from the same origin as the stablization of delta-Pu relative to alpha-Pu: namely, the partial localization of plutonium's 5f electrons.

2:00 PM *DD7.2
Research on 5f systems: from the basic to the useful. Gerry H. Lander, European Commission, Institute for Transuranium Elements, Karlsruhe, Germany.

The 5f elements present a great challenge to experimentalists and theorists alike. This talk will focus on the work performed at the Institute for Transuranium Elements (ITU) in Karlsruhe. Our "basic" research covers efforts to understand the properties of actinide elements and compounds, for example, by examining their properties under pressure, temperature, or at intense laser power. Of interest is the nature of their structural, electronic, and nuclear transitions; for example, the superconductivity of the new family of Pu compounds, as well as that of the element Am. We have our own in-house equipment as well as using large facilities such as neutrons, muons, lasers and synchrotron x-rays. Some of these results will be discussed. On the "useful" side of research I will discuss recent experiments to separate Am/Nd in the pyroprocessing process, new methods for analyzing actinides in the enviroment, and our progress in alpha-immunotherapy using alpha-emitting nuclides.

2:30 PM DD7.3
Localized and Itinerant 5f Electrons in Pu Compounds. John Joyce, John Wills, Tomasz Durakiewicz, Martin Butterfield, Elzbieta Guziewicz, John Sarrao, Al Arko, Luis Morales and David Moore; Los Alamos National lab, Los Alamos, New Mexico.

We report the electronic structure of Pu metal and several Pu compounds including magnetic (PuSb2, Pu2RhGa8) and superconducting (PuCoGa5) materials. Photoelectron spectroscopy (PES) was conducted at T of 10-80 K with a resolution between 35 to 75 meV. The electronic structure calculations are a mixed level model (MLM) which is an extension of the generalized gradient approximation within density functional theory. As determined both experimentally and computationally, the 5f electrons of plutonium exhibit two different configurations, one localized and the other

hybridized or itinerant. The dual nature of the Pu 5f electrons indicates a boundary between localized and itinerant in the actinides. The Pu 5f electrons exhibit this dual behavior over a wide ligand and crystal structure range. The PES measurements were carried out using the Laser Plasma Light Source at LANL. The samples were cleaned by laser ablation at low temperature. This method of surface preparation compares well with other methods of surface preparation including thin films. Seven different Pu compounds as well Pu metal have been measured. We observe a common electronic structure based on the dual nature of the Pu 5f electrons which fits many but not all of the Pu materials. This common electronic structure is observed in δ-Pu (non-magnetic), PuSb2 (magnetic transitions believed to be antiferromagetic), PuCoGa5 (superconducting below 18.5 K), PuIn3 ($\gamma \sim 100$ mJ/mole K2) and PuSn3. While this broad range of Pu materials exhibit a common electronic structure with the 5f electrons in a dual capacity, the details of the electronic structure, particularly in the vicinity of the Fermi energy (EF) are distinct for each material. Of the five Pu materials detailed above, PuSb2 has the narrowest quasi-particle peak near EF. This peak is $\sim$ 70 meV wide while the other materials including δ-Pu show peaks near EF of 100 meV or more. The narrow peak in PuSb2 is very close to but not at EF, possibly a hallmark for magnetic vs. enhanced-mass ground states in f-electron materials. The photoemission data for δ-Pu, PuSb2, PuIn3 and PuCoGa5 are compared against MLM calculations. The MLM is a framework for addressing the dual nature of the Pu 5f electrons where some of the 5f electrons are localized and do not participate in the bonding while the remainder of the 5f manifold is allowed to hybridize with the conduction electrons and participate in the bonding. Within the MLM, one obtains a good volume and a total energy minimum with 4 of 5 Pu 5f electrons localized. Furthermore, the calculations with 4 of 5 5f electrons localized agree well with the photoemission spectra. The broad range of Pu materials now being investigated combined with the successes of the mixed level model to describe the electronic structure are leading to a new understanding of Pu electronic properties. This work was supported by the U.S. Department of Energy.

2:45 PM DD7.4
Defect based spin mediation in δ-phase plutonium.
Michael Fluss, Lawrence Livermore National Laboratory, Livermore, California.

It has recently been shown, through an analysis of magnetic susceptibility and electrical resistivity data of δ-stabilized plutonium[1], that the hypothesis of a Kondo effect[2] ($T_K \sim$200-300K) in δ-plutonium is extant, thus implying that 5f electrons are localized as in the case of other known concentrated Kondo systems. However, although explaining the origin of the anomalous resistivity in δ-stabilized Pu(Al), the first principle origin of the pure Pu δ-phase remains as an unsolved problem. Recent theoretical work[3] , based on dynamical mean field theory (DMFT), suggests that the δ-phase and the α-phase of plutonium are two sides of the delocalization-localization knife-edge, total energies differing by only a few 10^{ths} of an eV. In this picture, the α-phase is not a weakly correlated phase; it is just slightly on the delocalized side of the localization-delocalization transition. Here, the δ-phase is intrinsically stable while the alloy-stabilized fcc binary alloys (e.g., Pu(Al) or Pu(Ga)) are the consequence of a "destabilization" of the α-phase by small amounts of impurities. In this presentation we will suggest a new related mechanism of defect based spin mediation stabilization of the pure Pu δ-phase due to equilibrium vacancies, predicated on our discovery of Kondo-like impurity behavior for vacancies in δ-phase Pu(Ga)[4]. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. 1. S. Meot-Reymond and J.M. Fournier, J. Alloys and Compounds, 232 (1996) 119 2. J. Kondo, Prog. Theor. Phys., 32, (1964) 37; ibid, Solid State Physics, 23, (1969) 184. 3. S. Y. Savrasov, G. Kotliar and E. Abrahams, Nature, 410 , (2001) 793 4. M. J. Fluss, et al. Kondo Behavior of Defects from Ion-Irradiation in Pu(Ga), UCRL-JC-145436 (2001) and UCRL-JC-153046 (2003)

3:30 PM *DD7.5
Fermi Liquid Instabilities and Superconductivity Near Quantum Critical Points in f-electron Materials.
M. Brian Maple, [1]Physics, University of Calif., San Diego, La Jolla, California; [2]Institute for Pure and Applied Physical Sciences, University of Calif., San Diego, La Jolla, California.

Landau's Fermi liquid theory is one of the cornerstones of condensed matter physics. The theory provides a description of the normal state physical properties of liquid ^{3}He, most metallic elements, compounds and alloys, and even metallic heavy fermion rare earth and actinide compounds that have enormous electron effective masses as high as several hundred times the free electron mass. Within the past two decades, several classes of materials characterized by strong electronic correlations have been identified in which the Landau Fermi liquid paradigm appears to be violated. A particularly interesting class of materials that exhibit such "non-Fermi liquid" behavior in their physical properties at low temperatures consists of certain compounds containing the f-electron elements Ce, Yb, or U. The non-Fermi liquid behavior appears to be associated with a zero temperature quantum critical point, which can originate from either single ion or inter-ionic interaction mechanisms. In several of these f-electron materials, superconductivity has been observed in the vicinity of a magnetic quantum critical point that can be accessed by varying a control parameter such as applied pressure or composition, suggesting that superconducting electron pairing is mediated by spin fluctuations, rather than phonons. In this talk, we describe the results of recent experiments on non-Fermi liquid and novel superconducting states that occur in the vicinity of quantum critical points in several f-electron systems based on Ce and U. This research was supported by the U.S. Department of Energy under Grant No. DE FG03-86ER-45230 and the National Science Foundation under Grant No. DMR 00-72125.

4:00 PM *DD7.6
The role of local disorder in non-Fermi liquid f-electron intermetallics. Corwin H. Booth, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The most interesting physics in condensed matter systems often arises from competing interactions. For instance, intriguing behavior develops in rare-earth/actinide intermetallic materials where the competition is believed to be between two different kinds of magnetic effects, namely, the RKKY and Kondo interactions. When disorder in the magnetic interaction strengths is considered, one can obtain a variety of ground states, including magnetic, spin glass, and Anderson lattice ground states. In addition, when the RKKY and Kondo interactions are approximately the same strength, a poorly understood low temperature state develops that exhibits few of the properties expected from the fundamental theory of metals, namely, Fermi liquid theory. Does this behavior signal a new, non-Fermi liquid (NFL) state of matter? Or is there a simpler explanation that involves only Fermi liquid ideas? Our group has been studying the role of disorder in systems that exhibit each of these ground states. I will present data demonstrating the degree of lattice disorder both on a local and a nanometer scale on systems such as Yb1-xLuxAl3, URh2Ge2, U3Ni3Sn4, UCu4Pd and CeRhRuSi2. Results are considered in light of various theories, especially for the latter three NFL materials.

4:30 PM *DD7.7
Uranium Compounds At High Pressures And Magnetic Fields. Andrew L. Cornelius, Department of Physics, University of Nevada, Las Vegas, Las Vegas, Nevada.

Correlated-electron systems are so named due to strong interactions between electrons unlike traditional metals (e.g. copper) that have "free electrons" that interact very weakly. Knowledge of the Fermi surface, density of electron states and band structure are the starting points for a first-principles understanding of the electronic and electronically related macroscopic properties, e.g. equation of state. The use of high pressure and high magnetic fields to alter the electron-electron (hybridization) and electron-lattice interactions give us powerful tools to understand complicated rare earth and actinide correlated-electron systems and allows precise testing of experiment to theory. Correlated-electron systems yield a wide variety of ground states that are a direct result of the hybridization strength including: short and long range magnetic order, spin fluctuating, enhanced Pauli paramagnetism, heavy fermion behavior and superconductivity. I will review some results on U compounds in high magnetic fields and high pressures. By comparing the results to Ce compounds that have significantly more localized f electrons, the effect of direct 5f electron wavefunction overlap in U compounds can be discerned. Consequences on the search for heavy fermion superconducters will be discussed.