SYMPOSIUM JJ

Actinides–Basic Science, Applications, and Technology

November 28 - December 1, 2005

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* Invited paper

SESSION JJ1: Electronic Structure Theory
Chairs: John Sarrao and Adam Schwartz
Monday Morning, November 28, 2005
Independence E (Sheraton)

8:15 AM Welcome and Introduction

8:30 AM *JJ1.1
Introduction to First-Principles Electronic Structure Methods: Application to Actinide Materials. John E. Klepeis, Lawrence Livermore National Laboratory, Livermore, California.

Actinide materials represent a significant challenge for modern first-principles electronic structure methods. In the early actinides the f-electrons are itinerant while in the late actinides they are strongly localized. In this talk I will give an introduction for non-experts to the major first-principles methodologies that are used in the study of actinide materials. In addition to providing general descriptions of each methodology I will give examples of their application to actinide materials and also indicate their relative strengths and weaknesses. I will describe a number of different methods that fall into the general category of those based on density-functional theory (DFT) within the local density approximation (LDA), including extensions such as the generalized gradient approximation (GGA). In this category there are a number of variants that can be divided further into two groups: (1) all-electron methods that explicitly include the core electrons [e.g. Linear Muffin Tin Orbital (LMTO) and Linear Augmented Plane Wave (LAPW) methods] and (2) pseudopotential-based methods that replace the core electrons with an effective ionic potential. The second general category of first-principles methods that I will describe attempts to go beyond the static mean field approximation of LDA-based calculations [e.g. Dynamical Mean Field Theory (DMFT)]. Throughout this talk particular emphasis will be placed on providing the appropriate background to enable the non-expert to gain a better appreciation of the application of first-principles electronic structure methods to the study of actinide materials. UCRL-ABS-213035. 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.

9:00 AM *JJ1.2
Phase Stability in f-Electron Materials from First-Principles Theory. Per Soderlind, Physics Department, LLNL, Livermore, California.

The structural stability in f-electron materials are studied by means of density-functional theory. In particular, pressure-induced phase transitions are predicted and compared with available experimental data. These transitions are explained by electronic-structure effects related to narrow f bands close to the Fermi level. Examples from both the rare-earth metal and actinide series will be presented. Recent studies include U, Pu, Am, Cm, and Bk. In addition the stability of fcc Pu and fcc Pu-Am system will be 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.

9:30 AM JJ1.3
Abstract Withdrawn

9:45 AM JJ1.4
Density Functional Theory Calculations on Pu-Ga Alloys. Shao-Ping Chen, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have used density functional theory to calculate the elastic, magnetic, and cohesive properties of fcc Pu-Ga alloys. The dependence of the properties on the Ga concentration from 0 to 25% will be presented. Some anomalies in the elastic properties have been found. The sensitivity of the properties to the correlation effects through on-site U and magnetic interactions will be discussed.

10:30 AM *JJ1.5
Localization of 5f electrons and phase transitions in americium. Michel H. Penicaud, DAM - Ile de France, Commissariat a L'Energie Atomique, Bruyeres-le-Chatel, France.

Density-functional electronic calculations have been used to investigate the high-pressure behavior of americium. The phase transitions calculated agree with the recent sequence obtained experimentally under pressure: double hexagonal close packed → face centered cubic → face centered orthorhombic → primitive orthorhombic. In the first three phases the 5f electrons are found localized, only in the fourth phase (Am IV) the 5f electrons are found delocalized. The localization of the 5f electrons is modelled by an anti-ferromagnetic configuration which has a lower energy than the ferromagnetic ones. In this study the complex crystal structures have been fully relaxed.

11:00 AM JJ1.6
5f Delocalization of Bulk fcc Americium and the (111) Surface: FP-LAPW Electronic Structure Calculations. D. A. Gao and Asok Kumar Ray; Physics, University of Texas at Arlington, Arlington, Texas.

The electronic and geometrical properties of bulk fcc americium and the (111) surface have been investigated with the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k suite of programs. In the WIEN2k code, the alternative basis set APW+lo is used inside the atomic spheres for the chemically important orbitals that are difficult to converge, whereas LAPW is used for others. The local orbitals scheme leads to significantly smaller basis sets and the corresponding reductions in computing time, given that the overall scaling of LAPW and APW + lo is given by N3, where N is the number of atoms. Also, results obtained with the APW + lo basis set converge much faster and often more systematically towards the final value. For relativistic effects, core states are treated fully relativistically and for valence states, two levels of treatments are implemented: (1) a scalar relativistic scheme including the mass-velocity correction and the Darwin s-shift and (2) a fully relativistic scheme with spin-orbit coupling included in a second-variational treatment using the scalar-relativistic eigen-functions as basis. For the bulk calculations, a fcc unit cell with one atom is used. A constant muffin-tin radius (Rmt) of 1.95a.u and plane-wave cut-off Kmax determined by RmtKmax=10.0 are used for all calculations. The Brillouin zone is sampled on a uniform mesh with 104 irreducible K-points for fcc bulk americium. The (111) surface is modeled by periodically repeated fcc Am surface slabs. Sixteen irreducible K points have been used for reciprocal-space integrations in the surface calculations. The study is carried out at different theory levels of approximations: (1) non-spin polarization vs. spin polarization; (2) scalar-relativity vs. full-relativity; (3) local-density approximation (LDA) vs. generalized-gradient approximation (GGA). Our results indicate that both spin polarization and spin orbit coupling play important roles in determining the geometrical and electronic properties of both bulk fcc americium and the (111) surface. In general, LDA is found to underestimate the equilibrium lattice constant and give a higher total energy compared to GGA results. While spin orbit coupling shows a similar effect on the surface calculations regardless of the model, GGA versus LDA, an unusual spin polarization effect on surface calculations is found in the LDA results as compared with the GGA results. The 5f delocalization transition of americium is employed to explain our observed unusual spin polarization effect. In addition, the quantum size effects in the surface energies and the work functions of the (111) fcc americium ultra thin films (UTF) are also examined. This work is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Department of Energy (Grant No. DE-FG02-03ER15409) and the Welch Foundation, Houston, Texas (Grant No. Y-1525).

11:15 AM JJ1.7
First-Principles Calculations of the Properties of Point Defects in Alpha- and Delta-Pu. Babak Sadigh, Jess Sturgeon, Per Soderlind and Wilhelm Wolfer; Lawrence Livermore National Laboratory, Livermore, California.

We present extensive first-principles calculations (using spin-polarized density-functional theory within the generalized gradient approximation) of the formation energies and volumes of vacancies and self-interstitials in both the alpha and the delta phases of Pu. These calculations are performed in supercells containing up to 64 atoms. We find that lattice defects modify the local spin moments of the surrounding Pu atoms. We study the interaction of the point defects with Ga impurities in delta-Pu and will discuss the role of Ga stabilization on the point defect properties in delta-Pu.

11:30 AM JJ1.8
A First-Principles Study of the (111), (001) and (110) Surfaces of delta -Pu. Haoran Gong and Asok Kumar Ray; Physics, University of Texas at Arlington, Arlington, Texas.

Plutonium (Pu) is arguably the most complex metallic element and has attracted extraordinary scientific and technological interests because of unique properties. In this talk, we will present a comparative ab initio computational study of the electronic structure properties of the (111), (001), and (110) surfaces of delta - Pu, using the all-electron full-potential linearized-augmented-plane-wave (FP-LAPW) method. We have first optimized bulk Pu at six theoretical levels, namely non-spin-polarized-no-spin-orbit-coupling (NSP-NSO), non-spin-polarized-spin-orbit-coupling (NSP-SO), spin-polarized-no-spin-orbit-coupling (SP-NSO), spin-polarized-spin-orbit-coupling (SP-SO), antiferromagnetic-no-spin-orbit-coupling (AFM-NSO), and antiferromagnetic-spin-orbit-coupling (AFM-SO) and the calculated equilibrium lattice constants at different levels of approximation have been used in the surface properties calculations. For the bulk calculations, an fcc unit cell with four atoms is used with a constant muffin-tin radius (Rmt) of 2.70 a.u. The plane-wave cut-off Kcut is determined by Rmt Kcut = 9.0. The Brillouin zone is sampled on a uniform mesh with 104 irreducible K-points. The surfaces of fcc delta-Pu are modeled by periodically repeated slabs of up to seven Pu layers at the corresponding optimized bulk lattice constants and separated by a 60 a. u. vacuum gap. It is found out that AFM-SO is the ground state for all systems studied, and spin-polarization and spin-orbit coupling effects play important competing roles. Detailed comparative electronic structure results such as cohesive energies, incremental energies, surface energies, spin magnetic moments, spin-polarization energies, spin-orbit coupling energies, and work functions will be presented for all the surfaces up to and including seven layers. For the films at the ground state (AFM-SO), surface energy rapidly converges and the semi-infinite surface energies are predicted to be 1.16, 1.21, and 1.42 J/m2 for d-Pu (111), (001), and (110) surfaces, respectively, while the magnetic moments show an oscillating behavior, gradually approaching the bulk value of zero with increase in the number of layers. In addition, the work functions are predicted to be 3.41, 3.11, and 2.99eV for delta-Pu films and the work functions tend to exhibit oscillations when the number of layers is less than five. Thus a 3-layer film might be sufficient for computations of adsorption energies while a 5-layer film may be necessary for precise computations of adsorbate-induced work function shifts. Results will be compared with available data in the literature. This work is supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U. S. Department of Energy (Grant No. DE-FG02-03ER15409) and the Welch Foundation, Houston, Texas (Grant No. Y-1525).

11:45 AM JJ1.9

Relativistic Effects on the Equation-of-State and Phase Stability of the Light Actinides, Th-Pu. Alexander Landa and Per Soderlind; Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California.

We have studied the effect of spin-orbit interaction on the equation-of-state (EOS) and the bcc/fcc phase stability in the light actinide metals Th-Pu. The spin-orbit coupling (SOC) is implemented in the conventional approximate fashion as a perturbation in the full-potential linear muffin-tin orbitals method (FPLMTO) whereas in the exact muffin-tin orbitals method (EMTO) the exact fully relativistic four component Dirac equation is solved. We show that the SOC has the largest impact on the phase stability in Np and Pu although the effect is diminished as density increases. In addition, the approximate implementation of the SOC with scalar-relativistic (FPLMTO) basis functions compares very favorably with the exact treatment (EMTO) when the SOC on the scalar-relativistic *p*-basis function is excluded. 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 JJ2: Superconductivity

Chairs: Michael Fluss and James Tobin
Monday Afternoon, November 28, 2005
Independence E (Sheraton)

1:30 PM *JJ2.1

Electronic Structure Calculations of Electronic, Structural, and Magnetic Properties of Actinide 115 Compounds. John M Wills and Raquel Lizarraga; Los Alamos National Laboratory, Los Alamos, New Mexico.

Results of density functional calculations of structural, electronic, and magnetic properties will be reported for a variety of actinide compounds, in particular actinide 115 compounds. Electron correlation is included in these calculations through spin polarization (LSDA) as well as through LSDA plus other functional and model correlation inclusions. Calculations of structural properties and electronic properties such as photoemission spectra, electric field gradients, and the Knight shift, using different assumptions for electron correlation, are compared with experiment, and calculated energies and band structures are examined to elucidated trends between compounds.

2:00 PM *JJ2.2

Structural Tuning of PuMGa$_5$ Unconventional Superconductors. Eric D. Bauer[1], J. L. Sarrao[1], J. D. Thompson[1], L. A. Morales[1], F. Wastin[2], J. Rebizant[2], J. C. Griveau[2], P. Javorsky[2], P. Boulet[2], E. Colineau[2], G. H. Lander[2] and G. R. Stewart[3]; [1]Los Alamos National Laboratory, Los Alamos, New Mexico; [2]European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany; [3]Department of Physics, University of Florida, Gainesville, Florida.

The discovery of superconductivity in PuMGa$_5$ (M = Co, Rh) with transition temperatures of $T_c = 18.5$ K and 8.7 K, respectively, offers a new way in which to understand the complex electronic structure of plutonium. The 5f electrons of Pu in PuCoGa5 are neither fully localized nor fully itinerant; elements of both kinds of behavior manifest themselves in such properties as an effective moment $\mu_{eff} = 0.7\ \mu_B$, close to that expected for Pu^{3+} (0.84 μ_B) and an enhanced electronic specific heat coefficient $\gamma \sim 100$ mJ/mol-K^2 consistent with moderately heavy fermion behavior. Comparison to the unconventional heavy fermion CeMIn$_5$ (M = Co, Rh, Ir) superconductors reveals a striking similarity between the two families of superconductors, indicating that structural tuning plays an important role in optimizing superconductivity in these materials. Both families of superconductors have a linear variation of T_c with c/a with a nearly identical slope $d(\ln T_c)/d(c/a) \sim 100$ despite the order of magnitude increase in the transition temperature of the PuMGa$_5$ compounds, suggesting common physics between the two families of superconductors; namely, that the superconductivity is mediated by magnetic spin fluctuations, in agreement with recent nuclear magnetic resonance measurements. In this talk, the remarkable similarities of the various physical properties between the PuMGa$_5$ and CeMIn$_5$ superconductors will be discussed.

3:30 PM *JJ2.3

Superconductivity in the Actinides Systems: Pressure Effect on PuTGa$_5$ (T=Co, Rh) and Americium Metal. Jean-Christophe Griveau, Jean Rebizant, Franck Wastin, Eric Colineau, Frederic Jutier and G. H. Lander; ITU-JRC, Karlsruhe, Germany.

Here we report recent pressure studies on the magnetic and superconducting properties of AnTGa$_5$ (An=Np, Pu, Am − T=Co, Rh, Ir) and Americium metal down to 0.4 K. Recent discovery of superconductivity in the Plutonium based compounds PuTGa$_5$ (T=Co, Rh) has shed a new light on the study of Actinides compounds. The fact that these systems present a lots of similarities with the CeTIn$_5$ (T=Co, Rh, Ir) such as their large superconducting domain regarding composition variation or the surprising law relating linearly crystallographic parameters and superconducting transition temperature T_c ($\Delta\ln(c/a) \sim T_c$) must not hide some fascinating features of these materials : they display superconducting characteristics one order of magnitude higher than their Cerium counterparts or all *5f* Superconducting Heavy Fermions ($T_c \sim 18.5$ K for PuCoGa$_5$ and ~9 K for PuRhGa$_5$ and $H_{c2} \sim 72$ T and 34 T respectively). Moreover they present at ambient pressure a Non Fermi Liquid described by a $T^{4/3}$ law which seems to maintain up to the highest pressure achieved (~20 GPa) for the 2 Plutonium superconductors. This is a characteristic feature as the lack of magnetic order observed through magnetization, resistivity or specific heat. Recent studies by NQR and NMR confirm that superconductivity is probably mediated by unconventional mechanism such as magnetic spin fluctuations. Finally we report superconducting pressure diagram of Americium metal under pressure up to 27 GPa and down to 0.4 K. By determination of the critical field $H_c(T)$ under pressure, we extract superconducting features of high pressure phases of Americium : this non magnetic element ($5f^6$, J=L+S=0) seems to become Type II superconductor under pressure ($H_c \sim 1$ T at 6 GPa). The complex superconducting diagram $T_c(p)$ related to the several phases transition led us to examine the localization delocalisation aspect of the 5f electrons in this metal through the Mott transition.

4:00 PM JJ2.4

Theory of the Knight Shift and Spin-Lattice Relaxation Rate in Pu-115 Compounds. Yunkyu Bang[3], Matthias J. Graf[1], Nicholas J. Curro[2] and Alexander V. Balatsky[1]; [1]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]MST Division, Los Alamos National Laboratory, Los Alamos, New Mexico; [3]Department of Physics, Chonnam National University, Kwangju, South Korea.

We calculated the Knight shift and spin-lattice relaxation rate for the Co and Rh Pu-115 compounds assuming a d-wave superconducting gap in the presence of strong impurity scattering. We discuss the implications for recent measurements of the spin-lattice relaxation rate in PuRhGa5 by Sakai and coworkers and present a prediction for the corresponding Knight shift. Furthermore, we notice a significant round-off of the spin-lattice relaxation rate 1/T1 just above the superconducting transition temperature that is not observed in the sister compound PuCoGa5. It appears that in both Pu-115 compounds superconductivity is mediated by spin fluctuations with similiar scaling behavior in the normal state.

4:15 PM **JJ2.5**
What Does the Specific Heat of Actinides at Low Temperatures Reveal? From Pa, Pu, and Am to $\mathbf{NpBe_{13}}$, $\mathbf{PuAl_2}$, and $\mathbf{PuGa_3}$ to Recent Work on $\mathbf{NpCu_{5-x}(Pd,Ni)_x}$ Alloys. G. R. Stewart[1], J. S. Kim[1], R. E. Sykora[2] and R. G. Haire[2]; [1]Physics, University of Florida, Gainesville, Florida; [2]CSD, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Measurements of the specific heats of metals at temperatures low enough to separate the electronic from the lattice contributions can provide valuable information regarding the density of electronic states at the Fermi energy. Specific heat can as well be a useful probe of magnetic (and other) transitions by revealing the entropy associated with the ordering. There are technical problems in determining the sample temperature caused by the radioactive self-heating; samples containing ^{238}U have negligible self-heating and can be measured to below 0.05 K, those with ^{237}Np or ^{242}Pu are measurable in small sample calorimeters to 0.5-2 K, while samples containing isotopes with higher specific activities (e. g. those with ^{231}Pa, ^{239}Pu, or ^{243}Am) may be difficult to cool to low enough temperatures to clearly separate the electronic from the lattice specific heat. After a brief review of some of the more interesting results on actinide elements and compounds to date, new results on the Np analogs of $UCu_{5-x}(Pd,Ni)_x$ will be presented. These results make clear the value of examining transuranium materials for furthering the understanding of highly correlated f-electron physics.

SESSION JJ3: Electronic Structure - Experiments
Chairs: John Klepeis and John Wills
Tuesday Morning, November 29, 2005
Independence E (Sheraton)

8:30 AM ***JJ3.1**
Probing the Boundaries of Localization in Metallic 5f Systems. John Joyce, Los Alamos National Lab, Los Alamos, New Mexico.

The dual nature of the 5f electrons in actinide materials is examined. Photoelectron spectroscopy results for several Pu materials, including the cubic δ-phase metal and the superconductor $PuCoGa_5$, give indication of the 5f electrons exhibiting both localized and itinerant character. We present experimental and theoretical results for the duality of the 5f electrons. The dual nature of the Pu 5f electrons clearly separates the boundary between localized and itinerant 5f character in the actinides. The Pu 5f electrons exhibit this dual behavior over a wide ligand and crystal structure range. The photoemission (PES) data for δ-Pu, $PuIn_3$, $PuSb_2$, and $PuCoGa_5$ are compared against model calculations. While there are a large number of Pu compounds which fit the model of 5f electrons in two configurations, there are notable exceptions which include paramagnetic PuTe and magnetic PuSb where the magnetic character would appear to be well localized. Within these bounding case, we observe from the photoemission results, a dual nature to the Pu 5f electrons in α- and δ-Pu metal, as well as $PuIn_3$, $PuSb_2$, $PuSn_3$, Pu_2RhGa_8 and $PuCoGa_5$. The calculations are a mixed level model (MLM) which is a multi-electron extension of the generalized gradient approximation. Using the MLM, one obtains good agreement for the volume and total energy minimum with 4 of 5 Pu 5f electrons localized. The calculations also agree well with the PES spectra. Comparisons will be made for different computational schemes for both δ-Pu and $PuCoGa_5$ as well as a general assessment of the electronic structure for Pu materials.

9:00 AM ***JJ3.2**
Effect of the 5f states on the symmetry of face-centered cubic delta plutonium. Kevin Thomas Moore[1], Adam Schwartz[2], Per Soderlind[2] and David Laughlin[3]; [1]Chemistry and Matrials Science, Lawrence Livermore National Labs, Livermore, California; [2]Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California; [3]Materials Science and Engineering Department, LCarnegie Mellon University, Pittsburgh, Pennsylvania.

Face-centered cubic delta-plutonium is the most anisotropic metal belonging to the 225 space group. This directly results from the bonding of the 5f states, which produce bonds between the 12 nearest neighbors with greatly varying strengths. Here, we will show that this causes a degradation of FCC symmetry, and that the idea of centrosymmetry when considering face-centered cubic delta plutonium may be faulty. We will advance this idea through crystallographic arguments, then discuss how this in turn affects the macroscopic properties that we observe, such as elastic constants, shear modulus, and phase transformations.

9:30 AM **JJ3.3**
Improving the Energy Resolution of Actinide Electron Energy Loss Spectra. Edgar Colin Buck, Rick Wittman and John Abrefah; Environmental Technology Division, Pacific Northwest National Laboratory, Richland, Washington.

State-of-the-art instrumentation for actinide research is often unavailable such as a monochromator electron beam source for TEM that have an energy resolution <0.2 eV. In this study, we used a conventional TEM (JEOL 2010) with a LaB6 electron source (energy resolution ∼0.8 eV at 200 keV) and attached image filter for conducting electron energy-loss spectroscopy (EELS) and used mathematical spectral sharpening routines to improve the visibility of EELS features. The main advantage of TEM-EELS over other spectroscopic methods, such as XAS or XPS is that the electronic density of states in an extremely small volume of material can be probed. Furthermore, because of the high spatial resolution in TEM, analyses from very fine grained and/or heterogeneous materials can be achieved with confidence. However, direct comparison of TEM-EELS with XAS or XPS data indicates, the energy resolution is still relatively poor with a conventional TEM system. We adopted the Richardson-Lucy (RL) (maximum-likelihood deconvolution) method to improve the resolution of acquired N-edge and M-edge actinide (uranium and neptunium) spectra. With the high intensity required to collect actinide spectra, obtaining the necessary point spread function proved difficult. However, under suitable conditions and after 50 RL-iterations the spectra resolution was improved to allow more accurate analysis of low level constituents in the analyzed actinide solids. We examined the advantage of running the R-L deconvolution on second difference spectral images of actinides for spectral sharpening and resolving minor peaks of interest. The technique shows great promise for revealing features that would normally only be accessible to higher energy resolution instruments.

9:45 AM **JJ3.4**
Spectroscopic Signature of Aging in delta-Pu(Ga). Brandon Chung, Adam J. Schwartz, Bartley B. Ebbinghaus, Mike J. Fluss, Jeffery J. Haslam, Kerri J..M. Blobaum and James G. Tobin; 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 nanoscale internal defects. The self-irradiation induced defects come in the form of Frenkel-type defects (vacancies and self-interstitial atoms), helium in-growth, and defect clusters. At present there are neither experimental nor theoretical models describing the changes in the electronic structure caused by the aging in Pu. This fact appears to be associated primarily with the absence of reasonably convincing spectroscopic evidence of the changes. This paper demonstrates that Resonant Photoemission, a variant of Photoelectron Spectroscopy, has strong sensitivity to aging of Pu samples. The spectroscopic results are correlated with an extra-atomic screening model [1], and are shown to be the fingerprint of mesoscopic or nanoscale internal damage in the Pu physical structure. This means that a spectroscopic signature of internal damage due to aging in Pu has been established. 1. P.A. Dowben, Surface Science Reports, v40, p151 (2000). 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

10:30 AM ***JJ3.5**
Determining the Electronic Structure of Pu using Unorthodox Spectroscopies. James Gerard Tobin, CMS, LLNL, Livermore, CA, California.

The standard method to determine the band structure of a condensed phase material is to (1) obtain a single crystal with a well defined surface and (2) map the bands with angle resolved photoelectron spectroscopy (occupied or valence bands) and inverse photoelectron spectroscopy (unoccupied or conduction bands). Unfortunately, in the case of Pu, the single crystals of Pu are either nonexistent, very small and/or having poorly defined surfaces. Furthermore, effects such as electron correlation and a large spin-orbit splitting in the 5f states have further complicated the situation. Thus, we have embarked upon the utilization of unorthodox electron spectroscopies, to circumvent the problems caused by the absence of large single crystals of Pu with well-defined surfaces. The talk will include a discussion of resonant photoelectron spectroscopy [1], x-ray absorption spectroscopy [1,2,3,4], electron energy loss spectroscopy [2,3,4], Fano Effect measurements [5], and bremstrahlung isochromat spectroscopy [6], including the utilization of micro-focused beams to probe single-crystallite regions of polycrystalline Pu samples. [2,3,6] This work was performed under the auspices of the U.S. DOE by Univ. of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48. 1. J.G. Tobin, B.W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G.D. Waddill, and G. Van der Laan, Resonant Photoemission in f-electron Systems: Pu and Gd, Phys. Rev. B 68, 1155109 (October 2003). 2. K.T. Moore, M.A. Wall, A.J. Schwartz, B.W. Chung, D.K. Shuh, R.K. Schulze, and

J.G. Tobin, The Failure of Russell-Saunders Coupling in the 5f States of Plutonium, Phys. Rev. Lett. 90, 196404 (May 2003). 3. G. van der Laan, K.T. Moore, J.G. Tobin, B.W. Chung, M.A. Wall, and A.J. Schwartz, ,Applicability of the spin-orbit sum rule for the actinide 5f states, Phys. Rev. Lett. 93, 097401 (Aug 2004). 4. J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, Competition Between Delocalization and Spin-Orbit Splitting in the Actinide 5f States, Phys. Rev. B 71, xxxxxx (2005). 5. J.G. Tobin, S.A. Morton, B.W. Chung, S.W. Yuand G.D. Waddill, Spin-Resolved Electronic Structure Studies of Non-Magnetic Systems: Possible Observation of the Fano Effect in Polycrystal Ce, submitted to Physica B, Proceedings of SCES05, Vienna, Austria, July 2005. 6. J.G. Tobin, M.T. Butterfield, N.E. Teslich Jr., R.A. Bliss, M.A. Wall, A.K. McMahan, B.W. Chung, A.J. Schwartz, Using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS) to Determine the Unoccupied Electronic Structure of Pu, submitted to the Royal Society of Chemistry, Proceedings of the Actinides 2005 Meeting, Manchester, UK, July 2005.

11:00 AM JJ3.6
Using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS) to Determine the Unoccupied Electronic Structure of Pu. Martin Butterfield, James Tobin, Nick Teslich, Annie Bliss, Mark Wall, Andy McMahan, Brandon Chung and Adam Schwartz; CMS, Lawrence Livermore National Laboratory, Livermore, California.

The investigation of the actinides is of great interest because of their unique electronic structure. At the pivotal point of the behavior of the electronic structure of the actinide series is plutonium. Pu has the most complex phase diagram of all metals, both with regard to the intricacy of the crystal structures and the number of different phases. While there are a number of ongoing experimental efforts directed at determining the occupied electronic structure of Pu, there is essentially no experimental data on the unoccupied electronic structure of Pu. We aim to determine the conduction band (unoccupied) electronic structure of Pu and other actinides in a phase specific fashion and emphasizing bulk contributions by using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS). BIS is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out). IPES can be used to follow the dispersion of electronic states in ordered samples. Owing to its low energies, IPES is usually very surface sensitive. However, by working at higher energies, we will sample preferentially for bulk properties, downgrading the impact of surface effects, following a philosophy similar to that of Mo et al.(1) Thus, from BIS, we would have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu. By using a nano-focused electron source associated with a SEM, we hope to gather phase specific information from crystallites within polycrystalline Pu samples. We will discuss the experimental arrangement required to carry out such an experiment and our progress in building such a system. This work was performed under the auspices of the U.S. DOE by University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48. (1) S.-K. Mo et al, Phys. Rev. Lett. 90, 186403.

11:15 AM JJ3.7
Studies of Structural and Electronic Properties of Actinide Compounds, by XANES Spectroscopy. Clara Fillaux[1], Christophe Den Auwer[1], Dominique Guillaumont[1], Eric Simoni[2] and Jerome Roques[2]; [1]DEN/DRCP/SCPS, CEA Marcoule, Bagnols sur Ceze, France; [2]Institut de Physique Nucleaire d'Orsay, Orsay, France.

Both structural and electronic properties of the actinide cations are of fundamental interest in order to describe the intramolecular interactions. The 5f and 6d orbitals are the first partially or totally vacant states of these elements and their properties reflect the nature of the actinide-ligand bond. Because of its chemical and orbital selectivities, XANES spectroscopy is useful to probe the actinide's frontier orbitals and then understand the cation reactivity towards chelating ligands. The L_3 edge (2p-6d transition) contains structural information on the coordination polyhedron because of important scattering features. But very little electronic information can be extracted, due to the short core hole lifetime, broadening the edge signal. On the other hand, the $M_{4,5}$ (3d-5f transition) and $N_{4,5}$ (4d-5f transition) edges provide a better resolution and allow us to achieve quantitative information. However, studies involving low energy transitions are scarce because of the technical difficulties related to the handling of radioactive compounds. Thus a multiple-edge approach has been chosen to study structural and electronic properties of actinides, such as electronic delocalization. XANES experimental spectra of molecular compound of uranium, neptunium and plutonium will be shown at L_3, $M_{4,5}$ and possibly $N_{4,5}$ edges. Experimental data analysis by simulating the absorption edge allows to compare the coordination polyhedrons, identify the electronic transitions and calculate the density of states associated with the absorption spectra. Moreover, a coupling between simulations of the experimental spectra and quantum chemical calculations is done, in order to improve the model describing the final states and better understand the bounding properties of the cation with the ligand.

11:30 AM JJ3.8
Temperature Dependence of Phonons and Elastic Constants in Pu and Ga-Doped Pu. Sven P. Rudin[1], S. Y. Hu[2] and M. I. Baskes[2]; [1]Group T-1, Los Alamos National Lab, Los Alamos, New Mexico; [2]Group MST-8, Los Alamos National Lab, Los Alamos, New Mexico.

The construction of modified embedded atom method (MEAM) models for pure and gallium-doped plutonium has been remarkably successful in light of the materials' complicated phase diagram and the model's relatively simple form. Among the successes are the model's ability to predict the relative phase stability of all phases correctly with the relative volumes close to the experimental values. The MEAM model is determined by fitting its parameters to a sequence of data; many of the parameters can be directly related to this data. However, the experimental data used to date does not fully determine the model. Additional improvement is achieved by comparing the results of simulations with experimental data, in particular by comparing phonons and elastic constants derived from the phonon dispersion curves. The phonons are calculated by extracting the dynamic structure factor from molecular dynamics (MD) simulations. By changing the energy in the simulation cell the temperature can be adjusted and the temperature dependence of the phonons and elastic constants extracted and compared with experiment. In, e.g., the face-centered cubic crystal structure the long wavelength modes are in good agreement with experiment as is expected from fitting the model to the elastic constants of the delta phase. The frequencies of zone-boundary phonons, on the other hand, depends on the short-range dynamics, which can thus be tuned by comparing the frequencies to experiment.

11:45 AM JJ3.9
Local Structure and Vibrational Properties of alpha-Pu, alpha-U, and the alpha-U Charge Density Wave.
Patrick G. Allen[1], Erik Nelson[1], Kerri Blobaum[1], Mark Wall[1] and Corwin Booth[2]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The local atomic environment and vibrational properties of atoms in monoclinic alpha-Pu as well as orthorhombic alpha-U and its low-temperature charge-density-wave (CDW) modulation are examined by extended x-ray absorption fine structure spectroscopy (EXAFS). Pu and U L_{III}-edge EXAFS data measured at low temperatures verify the crystal structures of alpha-U and alpha-Pu samples previously determined by x-ray diffraction and neutron scattering. Debye-Waller factors from temperature-dependent EXAFS measurements are fit with a correlated Debye model. The observed Pu-Pu bond Debye temperature of 162 K for alpha-Pu agrees with our previous measurement of the Debye temperature of the gallium-containing alpha'-Pu phase in a mixed phase alloy. The temperature dependence of the U-U nearest neighbor and second nearest neighbor Debye-Waller factors exhibits a sharp discontinuity in slope near T = 43 K, the transition temperature at which the charge-density wave (CDW) in alpha-U condenses from a soft phonon mode along the (100) direction. Our measurement of the CDW using EXAFS is the first observation of the structure of the CDW in polycrystalline alpha-U. The different temperature dependence of the Debye-Waller factor for $T < T_{CDW}$ can be modeled by the change in bond length distributions resulting from condensation of the CDW. For $T > T_{CDW}$, the observed Debye temperature of 199 K is in good agreement with other measurements of the Debye temperature for polycrystalline alpha-U.

SESSION JJ4: Actinide Materials
Chairs: John Joyce and Kevin Moore
Tuesday Afternoon, November 29, 2005
Independence E (Sheraton)

1:30 PM JJ4.1
The influence of extreme elastic anisotropy on defect properties. Wilhelm G. Wolfer, Alison Kubota and Babak Sadigh; Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California.

Properties of crystal lattice defects and of precipitates, which relate to their stress fields, are often estimated with isotropic elasticity. This is merely a matter of convenience as anisotropic stress calculations are very elaborate in practice, although well understood in principle. Unfortunately, there are very few elemental metals or alloys that possess elastic isotropy, tungsten being the lonely exception. When the elastic anisotropy is weak, it can be treated by perturbation methods with the zero-order approximation given by isotropic elasticity theory for optimally chosen effective elastic constants. For extreme elastic anisotropy, such as for the alkali metals and for δ-phase plutonium, analytical solutions or approximation are no longer possible for the elastic Green's function, and numerical approaches are required. The above materials mentioned with extreme elastic anisotropy are also positioned close to the borderline C12 = C44 where the elastic Green's function exhibits a singularity and beyond which the cubic lattice structure becomes unstable. Here, we employ the method of Barnett for the evaluation of the Green's function and its derivatives to study the influence of the large elastic anisotropy in δ-phase plutonium on the strain energies for its point defects, for its dislocations, and for coherent and incoherent precipitates. The elasticity results are complemented with those from atomistic simulations employing the modified embedded atom potential developed by Baskes for plutonium, and also with results from first-principle electronic structure calculations.

1:45 PM JJ4.2

Modeling the Static and Dynamic Aspects of Aging and Radiation Damage in delta-phase Plutonium using Molecular Dynamics Simulations. Alison Kubota[1], Wilhelm Georg Wolfer[1] and Maria-Jose Caturla[2]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Applied Physics, University of Alicante, Alicante, Spain.

Recently, there has been a great deal of interest in understanding the effect of radiation damage and aging in Pu. In particular, there has been many questions regarding the nature and the effect of point and extended defects such as voids and He bubbles on changes to electronic structure and phase stability. We will discuss recent results on cascade simulations in Pu using the Modified Embedded Atom Method (MEAM) potentials[1] to model the effect of 85 keV recoils that are produced during alpha decay. We performed energetic (5-85 keV) recoils in delta-phase Pu using these potentials to understand both the number and character of the defects produced. In general, these molecular dynamics simulations performed at 300K show cascades to produce a persistent amorphous structure unlike those observed in other "typical" face-centered cubic metals such as Al and Cu. In this work, we discuss how the angular-dependent electron density terms of the classical MEAM potential have important and profound effects on both the structure and behavior of point defects that are produced, and subsequently may have significant implications to other modeling and experimental efforts to understanding the aging of Pu. 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. References [1] Baskes, M. I., Phys. Rev. B, 62, 15532, 2000.

2:00 PM *JJ4.3

Emerging Magnetism Arising from Self Damage in α- and δ-Pu. Scott McCall, Michael J. Fluss, Brandon Chung, George Chapline, Michael McElfresh and Damon Jackson; Lawrence Livermore Nat'l Lab, Livermore, CA, California.

As a consequence of the unusual nature of plutonium's electronic structure, point- and extended-defects are expected to, and do exhibit extraordinary properties[1]. Low temperature magnetic susceptibility measurements on Pu and fcc-Pu(Ga) show that the magnetic susceptibility increases as a function of time, yet upon annealing the specimen returns to its initial magnetic susceptibility. This excess magnetic susceptibility (EMS) arises from the α-decay and U recoil damage cascades which produce vacancy and interstitials as point and extended defects. The temperature of the first annealing stage defines a temperature (<30K) below which we are able to characterize the time and temperature evolution of the accumulating damage cascades as being a saturation function. The temperature dependence of the EMS is well described by a time independent, Curie-Weiss like curve arising from a volumetric region surrounding each U damage cascade. This saturation picture also leads directly to a determination of the microscopic volume of the specimen that is affected by the frozen-in damage cascade. For our measurements in δ-Pu we calculate a diameter of the magnetically affected volume of $\sim$250$\acute{A}$ per damage cascade. This should be compared with an estimated volume that encloses the damage cascade itself (determined from molecular dynamics) of $\sim$100$\acute{A}$. Hence, the ratio of these volumes is $\sim$8. The observed anomalous magnetic behavior is likely a consequence of the highly correlated nature of the electrons. Similarities with defects in hole-doped superconductors[2] suggest a general phenomenon in strongly correlated electron systems, of which Pu may be a particularly unusual or special example. *This work was performed under the auspices of the U. S. DOE by Lawrence Livermore National Laboratory, under contract W-7405-Eng-48.* [1] M.J. Fluss, B.D. Wirth, M. Wall, T.E. Felter, M.J. Caturla, A. Kubota, T. Diaz de la Rubia, Journal of Alloys and Compounds 368 (2004) pp62-74 [2] F. Rullier-Albenque, H. Alloul, and R. Tourbot, Phys. Rev Lett., 91(4), 047001, 2003

3:30 PM JJ4.4

Thermodynamics of δ-Pu$_{(1-x)}$Ga$_x$ Alloys and Intermetallics. theresa lee, Ubaldo Gallegos, Michael Ramos, Ramiro Pereyra, Douglas Pete, Jeremy Mitchell and Luis Morales; Los Alamos National Laboratory, Los Alamos, New Mexico.

According to the American Pu-Ga phase diagram, the fcc δ-phase of Pu can be stabilized down to room temperature with the addition of anywhere between 2 and 9 at% Ga. According to the Russian Pu-Ga phase diagram, the fcc δ-phase of Pu is only metastable at room temperature in this composition range, and the thermodynamically stable state is a two phase mixture of α-Pu and the intermetallic Pu$_3$Ga. We have used high temperature solution calorimetry to determine the enthalpy of formation δ-Pu$_{(1-x)}$Ga$_x$ alloys at 25 °C. The enthalpy of formation of δ-Pu$_{(1-x)}$Ga$_x$ alloy with respect to the elements at 25 °C, $\Delta H_f{}^0$(25 °C), can be expressed as $\Delta H_f{}^0$(25 °C) = (2731.4x^2 - 405.6x + 8.3) kJ/mol, R^2 = 0.99. A strong negative deviation from ideality indicates that there is a strong thermodynamic driving force for ordering in the fcc δ-phase; this is consistent with the x-ray absorption fine structure spectroscopy studies of Cox et. al. The enthalpy of formation of δ-Pu$_{(1-x)}$Ga$_x$ alloy with respect to α-Pu and c-Pu$_3$Ga at 25 °C, $\Delta H_f{}^{\alpha,Pu3Ga}$(25 °C), is positive between 2.95 and 8.26 at% Ga, suggesting that the δ-phase is indeed only metastable, and that the thermodynamically stable state is a two phase mixture of α-Pu and Pu$_3$Ga. A definitive answer to which phase diagram is correct can only be found by comparing free energies of formation. Combining our enthalpy of formation data with the low temperature specific heat measurements of Taylor et. al., we find that the free energy of formation of δ-Pu$_{(1-x)}$Ga$_x$ alloy with respect to the elements at 25 °C, $\Delta G_f{}^0$(25 °C), can be expressed as $\Delta G_f{}^0$(25 °C) = (2731.4x^2 - 420.8x + 3.8) kJ/mol for $0.295 \leq x \leq 0.0826$. We eagerly await future measurements of the enthalpy, entropy, and free energy of formation of t-Pu$_3$Ga.

3:45 PM JJ4.5

Examination of the Kinetics of the Lower Temperature Solid-State Phase Transformations in Pure Plutonium. Dan S. Schwartz, Jeremy N. Mitchell and Ramiro A. Pereyra; NMT-16, Los Alamos National Laboratory, Los Alamos, New Mexico.

Differential scanning calorimetry and dilatometry were used to study the kinetics of the $\alpha\leftrightarrow\beta$ (125°C onset temperature) and $\beta\leftrightarrow\gamma$ (212°C onset temperature) solid-state phase transformations in high purity Pu. DSC analysis clearly shows that upon cooling from above the γphase field (>325°C) both the γ and β phases can be retained to room temperature. Phase retention appears to be strongly dependent upon the length of time spent in the γ phase field. The kinetics of the sluggish reversion of these retained phases was measured as a function of time spent in the α, β, and γ phase fields and will be discussed in detail. Metallography was used to examine the room temperature microstructures of specimens that were heated to different phase fields. A microstructural basis for the strong dependence of the reversion rate upon time spent in the α, β, and γ phase fields will be discussed. LA-UR-05-3947

4:00 PM JJ4.6

Evidence of Embryo Formation as a Precursor to the Delta to Alpha-Prime Transformation in a Pu-Ga Alloy. Kerri J. M. Blobaum[1], Christopher R. Krenn[1], Mark A. Wall[1], Thaddeus B. Massalski[2] and Adam J. Schwartz[1]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Materials Science and Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania.

It was experimentally observed that a single Pu-2.0 at% Ga sample can be thermally cycled many times, with nearly the same amount of transformation and reversion during each cycle, provided that the sample is annealed at 375°C for 8 hours and then conditioned at 25°C for at least 6 hours. The ambient conditioning period is crucial for obtaining the same amount of transformation to alpha-prime in each thermal cycle. Here, we present results from a series of experiments that investigate the effects of conditioning time and temperature on alpha-prime formation. When the sample is conditioned at 25°C for times between 0 and 6 hours, the amount of alpha-prime formed is a function of conditioning time. For conditioning treatments between 6 and 70 hours, however, the amount of alpha-prime formed is constant. Conditioning treatments at -50°C, 100°C, 150°C, 200°C, and 370°C all resulted in less alpha-prime formation than the 25°C treatments. We hypothesize that embryos of the thermodynamically stable alpha-phase form during the conditioning treatments, and these embryos serve as nucleation sites for alpha-prime upon subsequent cooling. This result is an indirect confirmation of the Russian Pu-Ga phase diagram. 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.°

4:15 PM JJ4.7

Magnetic and Resistive Properties of the Annealing of Radiation Damage in Pu and Pu Alloys. Michael J. Fluss, Scott McCall, Brandon Chung, George Chapline, Michael McElfresh and Damon Jackson; LLNL, Livermore, CA, California.

We report a high fidelity radiation damage-isochronal annealing curve based on changes in magnetic susceptibility for α-phase Pu from 5-350K with Stage-I annealing at $>$30K and complete annealing at $\sim$315K. These results, while based on changes in magnetic susceptibility, are surprisingly similar to resistivity data reported 40 years ago by Wigley (Proc. R. Soc. A 284 (1964) 344) and suggest the excess magnetic susceptibility (EMS) is the result of accumulated radiation damage. We also report the comparison of resistivity studies (M.J. Fluss et al, J. of Alloys and Compds. 368 (2004) pp(62-74) and new magnetization studies of radiation damage accumulation and annealing in fcc δ-phase Pu(3.3 at% Ga). This comparison, unlike the similar data for α-Pu, exhibits interesting differences, indicating that interstitials in δ-Pu do not contribute as strongly as vacancie do to the excess magnetic susceptibility. The possible role of vacancies in stabilizing the low-density δ-phase of Pu will be discussed. *This work was performed under the auspices of the U. S. DOE by Lawrence Livermore National Laboratory, under contract W-7405-Eng-48.*

4:30 PM JJ4.8

Spinodal ordering and precipitation in U-6wt%Nb.
Luke L. Hsiung and Jikou Zhou; Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California.

Low-temperature aging mechanisms in water-quenched U-6wt% (14 at%) Nb under the conditions of natural aging (25°C) and artificial aging (250°C) have been investigated. Both spinodal decomposition and order-disorder transformation are found to occur, and the transition sequence that occurs during isothermal aging is found to be dependent on aging temperatures. When isothermal aging at 200°C, the transformation sequence is proposed to be supersaturated solid solution α// -> spinodal decomposition -> α1 (Nb-depleted) + α2 (Nb-enriched) -> ordering transformation and precipitation -> disordered α (U) + ordered α^{o}. When isothermal aging at 25°C, the transformation sequence is proposed to be supersaturated solid solution α// -> ordering transformation -> α^{po} (partially ordered) -> phase decomposition and precipitation -> α (U) + ordered α^{o}. The precipitation of ordered α^{o} phase results in the precipitation hardening and ductility embrittlement of the alloy. 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.

SESSION JJ5: Poster Session: Actinides

Chairs: Eric Bauer and Kerri Blobaum
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

JJ5.1

Burst Martensitic Transformations in a Pu-Ga Alloy.
Kerri J. M. Blobaum[1], Jeremy N. Mitchell[3], Christopher R. Krenn[1], Mark A. Wall[1], Thaddeus B. Massalski[2] and Adam J. Schwartz[1]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Materials Science and Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania; [3]Los Alamos National Laboratory, Los Alamos, New Mexico.

Martensitic transformations can occur via two modes: thermoelastic and burst. In thermoelastic martensites, deformation can be accommodated elastically and transformations occur smoothly with changes in temperature or stress. Burst martensitic transformations require both elastic and plastic deformation to accommodate strain; individual martensite particles form at the speed of sound, and the overall accumulation of martensite may increase in discrete, incremental steps. Here, we examine a unique martensitic transformation and reversion in a Pu-2.0 at% Ga alloy and show evidence that they proceed via the burst mode. Upon cooling from ambient conditions, the metastable delta phase partially transforms martensitically to the alpha-prime phase with a volume contraction of 25%. This large volume change suggests a burst transformation. Furthermore, using differential scanning calorimetry, dilatometry, and resistometry, we have observed that the alpha-prime to delta reversion proceeds in discrete increments, which appear as steps in dilatometry and resistometry data and as sharp peaks in DSC data. This incremental progression is believed to be the result of autocatalytic cascades of many alpha-prime particles reverting nearly-simultaneously to the delta phase. Finite-element modeling suggests that residual stresses in the regions of reverted alpha-prime particles may catalyze (or retard) additional transformation. These stresses could initiate cascades of alpha-prime particles that revert nearly-simultaneously. The cascades are likely quenched by stress and/or temperature changes resulting from the transformation itself. During the forward delta to alpha-prime transformation, burst events are not observed with the above techniques. The transformation, however, is still expected to proceed via the burst martensite mode because of the large volume changes required. Because alpha-prime must be nucleated in the delta matrix before it can grow as an individual burst, the transformation may not occur cooperatively. These individual bursts may be too small to be resolved by the above techniques, and the signal observed corresponds to a cumulative total of all the events. 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.

JJ5.2

Isothermal Martensitic Phase Transformations in Plutonium-Gallium Alloys. Benoit Jean-Paul Oudot, Kerri J. M. Blobaum, Mark A. Wall and Adam J. Schwartz; Chemistry & Materials Science, Lawrence Livermore National Laboratory, Livermore, California.

Under ambient conditions, the thermodynamically stable phase of pure plutonium is the brittle monoclinic alpha phase. However, alloying plutonium with a few atomic percent of an element such as gallium or aluminum causes the malleable face-centered-cubic delta-phase to be retained at ambient temperatures. For Pu-Ga systems at ambient conditions, the delta-phase is metastable and gives rise to an extremely slow eutectoid decomposition to alpha + Pu$_3$Ga. When the metastable delta phase is cooled to sub-ambient temperatures, a partial transformation to the alpha-prime martensitic phase occurs. This alpha-prime phase is similar to the alpha-phase, but it has Ga trapped in the lattice. Previously we have studied the delta to alpha-prime phase transformation (at about -120°C) and its reversion (at about 30°C) using continuous cooling and heating cycles in a differential scanning calorimeter. Here, the thermodynamics and kinetics of the isothermal delta to alpha-prime phase transformation and its reversion in a Pu-2.0 at% Ga have been studied by holding in a differential scanning calorimeter at various temperatures. This delta to alpha-prime transformation is reported to have unusual double-C curve kinetics in a time-temperature-transformation diagram. The sub-ambient isothermal experiments give rise to a better understanding of transformation mechanisms that may result in double-C curve kinetics. Recently, we have observed that the alpha-prime to delta reversion can also occur under isothermal conditions. Isothermal reversion experiments demonstrate that the reversion occurs in bursts that are distributed randomly in time. Additionally, these experiments demonstrate the non-linear behavior of the transformation versus time and temperature. 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. The Commissariat a l/Energie Atomique (CEA) of Valduc is also acknowledged.

JJ5.3

Physical Property Changes in Plutonium from Accelerated Aging using Pu-238 Enrichment. Brandon Chung, B. William Choi, Stephen Thompson, Conrad Woods, David Hopkins and Bartley Ebbinghaus; Lawrence Livermore National Laboratory, Livermore, California.

The change in physical properties of plutonium-based alloys with self-irradiation damage is of significant interest to the Stockpile Stewardship Program. Plutonium-based alloys, because of its self-irradiation by alpha decay, ages by means of lattice damage, Frenkel-type defects and clusters, and helium in-growth. These integrated aging effects will result in microstructural and physical property changes. Because these effects would normally require decades to measure, studies are underway to asses the effects of extended aging on the properties of plutonium alloys by incorporating roughly 7.5 wt% of highly specific activity isotope 238Pu into the weapons-grade plutonium to accelerate the aging process. By monitoring the properties of the 238Pu accelerated alloy over a period of about 3.5 years, the aging properties of plutonium due to alpha decay in stockpile pits can be projected for periods up to about 60 years. This paper presents density, volume, lattice parameter, and tensile strength changes to spiked alloys. After thirty-six equivalent years of aging, the accelerated alloys at 35°C have swelled in volume by 0.12 to 0.14 % and now exhibit a near linear volume increase due to helium bubble in-growth. The average He-to-vacancy ratio was extracted to be about 2.5. The engineering stress of the alloys increases about 10% per decade of equivalent age. Increase in strength with age is expected from the helium bubble in-growth, which behave like precipitate hardening. 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

JJ5.4

Computer simulation study of self-irradiation effects in plutonium alloys. Lilian Berlu[1], Gaelle Rosa[1], Philippe Faure[1] and Gerald Jomard[2]; [1]DRMN/SEMP, CEA, Is-sur-Tille, France; [2]DPTA/SPMC, CEA, Bruyere le Chatel, France.

The study of self-irradiation effects on plutonium alloys cristallographic structure is of prime importance to determine the time evolution of their physical properties. The α decay of 239-plutonium leads to the formation of two nuclei (4-He and 235-U) with sufficiently high energy to eject plutonium atoms from their initial site in the metal[1-2]. These nuclei are responsible for numerous crystallographic point defects which emerge in the material from displacement cascades. These primary defects can then diffuse through the cristal, combine with each other to form clusters, and are responsible for macroscopic modifications of metal properties. Experimental measurements have shown that plutonium alloys properties could be affect by radiation damages. As an example, swelling of Pu alloys has been observed with aging with different techniques (dilatometry, X-ray diffraction). The process take place on different time and space scales which range from atomic and nanosecond to macroscopic and years, and cannot be achieved by a single molecular simulation methode. Consequently, a multi-scales approach, both in time and space, has been developed to study self-irradiation damages by computer simulations. This approach combines molecular dynamics(MD) for the atomic scale, mesoscopic Monte Carlo(MC) and kinetic rate calculations. The formation of primary defects following a 239-Pu decay is calculated using MD simulation of displacement cascades due to 235-U (PKA). Futher diffusion and recombinaition process of the defects formed is studied with mesoscopic scale simulations MC. Here we show recents results obtained by MD calculations. These simulations have been performed using the MEAM interatomic potential formalism [3]. The point defects formation is calculated using a progressive increase in the PKA energy. Futher calculations of physical properties are used to validate the simulations by comparing to experimental data. [1] P. Pochet, Nucl. Instruments and Methods in Physics Research B, 202 (2003) 82-87 [2] W.G. Wolfer, Los Alamos Science, 26 (2000) 275-285 [3] M.I. Baskes, Phys. Rev. B, 62 (2000) 15532-15537

JJ5.5

Molecular Dynamic Simulations of Phase Stability and Phase Transition Kinetics in Pu-Ga Alloys. Shenyang Hu, Mike Maskes and Marius Stan; MST8, Los Alamos National Laboratory, Los Alamos, New Mexico.

Plutonium (Pu) presents six different solid phases and a liquid phase as a function of temperature at zero pressure. Experiments demonstrate that small additions of Ga in Pu can stabilize the face-centered cubic δ-phase, a phase with superior mechanical properties. In this work, the molecular dynamics (MD) method was employed to study the phase stability and phase transition kinetics in Pu-Ga alloys. The atomic interactions are described by Modified Embedded-Atom Method (MEAM) potentials. The potential parameters were fitted with first principles data at 0K for Ga, and experimental data at 0K and elevated temperatures for Pu. Experimental data for the reference phase Pu3Ga (L12) was also used. The free energy and entropy differences between a reference state and an Einstein (harmonic) solid were calculated using the method of adiabatic switching in a MD formalism. Based on the MD results, the formation energies and equilibrium volumes of each phase were calculated. Analytic free energy functions were constructed in terms of Ga composition and temperature for predicting phase stabilities. Comparison between simulation results and the existing experimental phase diagram for pure Pu shows that they are in good agreement. With the developed MEAM potentials, the phase transition kinetics from δ phase to α phase was studied by simulating the growth behavior of an α nucleus in a δ phase matrix. The interfacial energies and interface structures and critical sizes were also investigated.

JJ5.6

Abstract Withdrawn

JJ5.7

The growth of epitaxial uranium oxide observed by micro-Raman spectroscopy. Nina Maria Caculitan and Wigbert J. Siekhaus; Dept of Materials Science and Chemistry, Lawrence Livermore National Laboratory, Livermore, California.

Raman spectroscopy can be performed with micrometer resolution and can thus be used to determine the dependence of oxide thickness on the substrate grain structure or local impurity inclusions. The Raman signal amplitude emitted from an epitaxial uranium oxide layer as a function of oxide thickness has been modeled for light of 632.8 nm wavelength incident on the oxide and reflected from the uranium substrate using the optical properties determined by spectrophotometry. The model shows that the Raman signal increases with oxide thickness and saturates at about 200 nanometer thickness. The model was compared with the measured Raman signal amplitude of an epitaxial uranium oxide layer growing in air with a known time dependence of oxide growth. 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.

JJ5.8

Time-resolved and CW Optical Studies of the Itinerant Antiferromagnet UNiGa5. Elbert Chia, Hae-Ja Lee, Richard Averitt, Eric Bauer, John Sarrao and Antoinette Taylor; MST-10, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have performed optical conductivity measurements on the itinerant antiferromagnet UNiGa5. We will show both (a) time-resolved data using a optical pump-probe technique, and (B) CW data using a Fourier Transform Infrared Spectrometer from the far-infrared to the ultra-violet range. Comparisons will be made to other data obtained from resonance and diffraction techniques.

JJ5.9

Uranium and Thorium for EUV and Soft X-ray Optics. R. Steven Turley and David Dean Allred; Physics and Astronomy, Brigham Young University, Provo, Utah.

Perhaps the most novel and exciting application of the actinide elements and their compounds to emerge in the last decade is as thin-film optical materials between 20 and 450 eV. This important portion of the electromagnetic spectrum has been difficult to utilize to date because of the high absorption which almost all materials possess. Uranium, thorium and their compounds are playing a special role. Our group has pioneered much of the practical work, which includes: 1. Preparing uranium/silicon multilayer-coated mirrors that orbit the earth in the EUV imager of the IMAGE spacecraft, returning motion pictures of the earth's magnetosphere. 2. Determining that uranium and thorium oxide thin films can be prepared with double the reflectivity of any other material at low angles for many portions of the important soft x-ray spectrum. 3. Measuring the optical constants of uranium and thorium oxide over portions of this range. 4. Confirming that the optical constants of uranium and thorium compounds are very different than those of other elements and their compounds over this range. Previous researchers reported very high deltas (1-n, where n is the real part of the index) and very low betas (absorption) for elemental uranium. The transparency of the uranium oxide is particularly important. We will discuss our design of a soft x-ray zone plate with greater than 25% power to the focal point. Our work has also lead to a better understanding of the surface oxidation of uranium and uranium nitride at room temperature and the stability of uranium and thorium oxide thin films under ambient conditions. We will review our work and report the most salient technological applications and basic science insights.

JJ5.10

Murataite Ceramics Doped with Lanthanides and Uranium. Sergey Stefanovsky[1], Sergey Yudintsev[2], Boris Nikonov[2] and Olga Stefanovsky[1]; [1]SIA Radon, Moscow, Russian Federation; [2]IGEMRAS, Moscow, Russian Federation.

Phase composition of the murataite-based ceramics containing 10 wt.% Ln, Ce, Nd, Eu, Gd, Y, Zr oxides and mixed oxides simulatinf rare earth/actinide fraction of high level waste was studied. The ceramics were prepared by melting of oxide mixtures in Pt ampoules in air at ~1500 oC. They are composed of predominant murataite-type phases and minor extra phases: rutile, crichtonite,perovskite, ilmenite/pyrophanite, and zirconolite (in the Zr-bearing sample only). Three murataite-related phases with five- (5C), eight- (8C), and three-fold (3C) elementary fluorite unit cell are normally present in all the ceramics. These phases form core, intermediate zone and rim of the murataite grains, respectively. They are predominant host phases for the rare earth elements and uranium whose concentrations are reduced in a row: M-5C $>$ M-8C $>$ M-3C. Appreciable fraction of La, Ce, and Pu enter the perovskite phase and may exist in a trivalent form.

JJ5.11

Crystal Structure of Uranyl Carboxylates. Paul Giesting, Nathan J. Porter and Peter C. Burns; Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana.

Uranyl-organic complexation in geologic fluids can have a profound impact upon uranium solubility and transport. Studies of uranyl organometallic crystal structures provide a basis for understanding complexation of the uranyl ion in solution. Novel uranyl oxalates The crystal structures of several novel uranyl oxalates, synthesized under mild hydrothermal conditions, have been determined. These structures demonstrate new features little seen or not previously known in this chemical system, in particular polymerization into infinite sheets and direct linkage of uranyl polyhedra. Further work on the chemistry of this and other systems of hexavalent uranium and low molecular weight carboxylic acids, especially formic acid, is likely to turn up new insights. Structural classification scheme for uranyl carboxylates Although a hierarchical scheme exists for classifying inorganic uranyl compounds (Burns et al. 1996), no similar work has been done for organic compounds. Such a hierarchy would have practical benefits, in particular making structural information more accessible and understandable to workers studying related problems such as the environmental transport of hexavalent uranium as dissolved organic complexes. We offer a simple scheme that classifies uranyl oxalate structures by analyzing the long-range structural features and the coordination environments of uranyl ions, which leads to a structural symbol that can be used to easily identify uranyl oxalates with common structural features. This system is equally applicable to other carboxylate complexes with the uranyl ion, and could be extended to apply to any organic complex of the uranyl ion. Burns, P. C., Miller, M. L., and Ewing, R. C. (1996). U6+ minerals and inorganic phases: A comparison and hierarchy of crystal structures. The Canadian Mineralogist, 34:845 - 880.

JJ5.12

Hydrothermal Syntheses, Structures, Ion-Exchange, and Optical Properties of Uranium-Based Materials.

Tatiana Y. Shvareva[1], James V. Beitz[2] and Thomas E. Albrecht-Schmitt[1]; [1]Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama; [2]Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

In this talk, we will present recent results from our group on the preparation, single crystal X-ray diffraction studies, ion-exchange properties, and NLO measurements of several new alkali metal/uranyl/M (M = Ga or transition metal)/phosphates. We will demonstrate new routes for synthesizing these compounds in high-yield in the form of large single crystals. Using single crystal X-ray diffraction, we have determined that these compounds adopt open-framework structures constructed from low-dimensional features. With judicious choice of transition metal, these compounds can also be made to be polar. These novel structures lend themselves to further measurements that include selective ion-exchange of the alkali metals for alkali earth metals, which may be relevant for the removal of ^{90}Sr from nuclear waste, and second-harmonic generation of frequency-doubled light.

JJ5.13

Polymer Assisted Deposition of Thin Metal Films: A New Technique to the Preparation of Metal Oxides, Metal Nitrides, Reduced Metal and Multi-Metallic Films.

Piyush Shukla[1], Anthony K. Burrell[1], T. Mark McCleskey[1], Quanxi X. Jia[2] and Yuan Lin[2]; [1]Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Material Science Technology, Los Alamos National Laboratory, Los Alamos, New Mexico.

Currently, there are a variety of techniques to deposit metal thin films ranging from high vacuum techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), through to solution methods like sol-gel. All of these techniques have their pluses and minuses. The vacuum techniques can be limited by size and cost. Sol Gel does not have these same limitations but is plagued by other problems related to difficulty in obtaining precursors and complications when complex stoichiometries are desired. Polymer assisted deposition (PAD) is a new method developed at the Los Alamos National Laboratory that is attempting to address some of the limitations of sol-gel and costs of high vacuum techniques. PAD utilizes an aqueous polymer to bind a metal or metal complex that can then be spin-coated or dip-coated onto any size or shape substrate. The polymer actively binds the metal and serves both to encapsulate the metal to prevent chemical reaction and maintain an even distribution of the metal in solution. This ensures a homogeneous metal distribution and prevents unwanted reactivity that can lead to the formation of undesired phases. These solutions can remain stable for months, even when multiple metals are used. In the PAD process, the polymer has dual functions. First, the controlled solution concentration and the molecular weight of the soluble polymer help achieve the desired viscosity. Second, the polymer functions as a binding agent to the metal precursor. The latter feature makes it possible to grow relatively thicker and crack-free films that are difficult or nearly impossible to prepare by sol-gel or chemical-solution deposition. Another advantage that PAD has over existing techniques is that the same solution can be used as precursors for the growth of metal oxide, metal nitride, or reduced metal films. This technique also allows for the easy preparation of multi-metallic films by simply mixing the solutions in the desired stoichiometries. Herein, we report on the preparation of a variety of metal oxide, metal nitride, reduced metal and multi-metallic systems using the PAD technique.

JJ5.14

Universal electronic intra-4f transition rate of erbium in solid hosts. Albert Polman, Center for Nanophotonics, FOM-Institute AMOLF, Amsterdam, Netherlands.

Photoluminescence spectroscopy can reveal detailed information on the local atomic scale environment of lanthanide and actinide ions. Here we present measurements of the photoluminescence spectrum and decay rate of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ intra-4f transition at λ=1.5 micron of optically active Er^{3+} ions in a broad range of materials, including dielectrics, ceramics and semiconductors. Data are shown for erbium implanted silica glass, sodalime silicate glass, phosphate glass, Al_2O_3, Y_2O_3, Si_3N_4, $LiNbO_3$, amorphous Si, crystalline Si, and silicon-rich SiO_2. The room temperature photoluminescence spectra for all materials are all distinctly different, reflecting clear variations in the local bonding nature, which is confirmed by EXAFS measurements on selected hosts. The luminescence lifetimes measured for all Er-doped hosts are also distinctly different, and range between 1 ms for the Si-based hosts to 24 ms for sodalime glass. According to Fermi's Golden Rule the luminescence decay can be described by the product of an electronic component and a photonic component, the latter being dependent on the local optical density of states and local field effects. We first correct the measured decay rates in all hosts by dividing out the local optical density of states, which depends on the host dielectric constant and position of the erbium ions in the host. Subsequently, a local field correction using either the Lorentz local field or the empty cavity model is applied, using the matrix dielectric constant as input parameters. Slight spectral shifts that are observed between different hosts are consistent with these local field corrections. Applying the density of states and local field corrections it follows quite surprisingly that the radiative decay rate in all materials (corrected to ϵ=1) is roughly identical: 30 s^{-1}. This then implies that the electronic component in Fermi's Golden Rule is similar in all hosts. Given the fact that the Er intra-4f transition is dipole forbidden, this implies that the factors that make the electron transition slightly allowed, e.g. a delocalization of the 4f shells, are identical in all hosts. Implications for the local environment of Er, other lanthanides and the actinides will be discussed.

JJ5.15

Extraction Separation of REE Isotopes in Non-Stationary Conditions. Alexey Alekseevich Kopyrin[1], Mikhail Alexander Afonin[1], Alexander Alexander Baulin[1] and Kenton J. Moody[2]; [1]Rare Earth, SPIT, Saint-Petersburg, Saint-Petersburg, Russian Federation; [2]Analytical and Nuclear Chemistry Division, Lawrence Livermore National Laboratory, Livermore, California.

High level wastes consist of long-live isotopes of medium elements. Some of these isotopes are of commercial interest, but problem of its chemical separation has not been solved - these isotopes usually deposited with other radioactive waste. The problem of isotope separation is very actual at nowadays. There are a lot of methods for isotope separation based on difference in physical properties and they are wide distributed in the industry (especially gas diffusion method). Methods based on the difference in chemical properties of isotopes (isotope effects) like isotope exchange reactions (thermodynamic isotope effects) and kinetic isotope effect are usually applied for separation of light isotopes, but in [1] it was written about industry applying of separation process of ^{235}U and ^{238}U isotopes based on the isotope exchange reaction (between valences 3 and 4) at the liquid-liquid extraction conditions (with using TBP) with isotope separation factor equal to 1,0023. In this work we represented data about possibility of isotope separation by oscillatory extraction. Experimental set up consisted of two extractors coupled by bulk liquid membrane (extractant - 0.5 M TBP in tetradecane). The oscillatory extraction method based on exaggerating the small kinetic differences between isotopes during competitive extraction driven by Belousov-Zhabotinsky (BZ) reaction. An oscillation of Ce(III) and Ce(IV) concentrations during BZ reaction induces oscillations of free extractant concentration. This leads to the difference in the partition of isotopes between aqueous phases and an organic phase. The organic phase is enriched by isotope with "quick extraction kinetic" and after stripping to the second aqueous phase it is enriched by this isotope also. The possible explanation of the results could be based on the fact that due to the difference on isotope properties in the kinetic of extraction and complexation there are differences in average concentrations of isotopes in the organic phase. Therefore the difference in the isotopes concentrations in different extractors appears. The separation of ^{142}Ce and ^{140}Ce isotopes between aqueous phases of two extractors coupled by bulk liquid membrane in the experiments with cyclic chemical oxidation/reduction with enrichment factor about 2.5% was observed. In the same conditions the separation of the Nd isotopes (heavy isotopes of Nd - ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd and ^{150}Nd from the light isotope - ^{143}Nd) in the same experiment with enrichment factor about 0.7-1.4% was observed. Acknowledgements. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under grant RC0-20000-SC14 and RUC2-20011-ST-04 administered by the Civilian Research and Development Foundation.

JJ5.16

Abstract Withdrawn

JJ5.17

Optical Absorption, Stability and Structure of $NpO_2{}^+$ Complexes with Dicarboxylic Acids. Guoxin Tian and Linfeng Rao; Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California.

Complexation of $NpO_2{}^+$ with oxalic acid (OX), oxydiacetic acid (ODA), iminodiacetic acid (IDA) and thiodiacetic acid (TDA), has been studied using spectrophotometry in 1 M $NaClO_4$. Both the position and the intensity of the absorption band of $NpO_2{}^+$ at 980 nm are affected by the formation of Np(V)/dicarboxylate complexes, providing useful information on the complexation strength, the coordination mode and the structure of the complexes. Both 1:1 and 1:2 complexes were observed with OX, ODA and IDA, but only 1:1 complex was observed with TDA. The stability of the 1: 1 complexes follows the order: TDA <¡ OX < ODA < IDA. The stability of Np(V)/TDA complex is quite low ($\log\beta_1 = 0.88$) and comparable to that of Np(V)/acetate complex, suggesting only one carboxylate group of TDA participates in the complexation. The much higher stability constants for the Np(V) complexes with OX, ODA and IDA indicate that both carboxylate groups coordinate with Np(V) in these complexes, with possible participation of the ether oxygen in ODA and the nitrogen in IDA. By nature, the absorption band of $NpO_2{}^+$ at 980 nm is a 5f - 5f transition that is allowed only if the $NpO_2{}^+$ species does not have an inversion center. Its intensity is thus sensitive to the equatorial coordination environment of $NpO_2{}^+$. It has an intensity of $\sim$ 395 $M^{-1}cm^{-1}$ for the free $NpO_2{}^+$ species in solution, $NpO_2(H_2O)_5{}^+$. Upon the formation of 1:1 complexes with OX, ODA and IDA, this band shifts to longer wavelengths but its intensity changes only slightly, suggesting the 1:1 complexes have a similar symmetry to that of $NpO_2(H_2O)_5{}^+$. On the contrary, the intensity of this transition is drastically different in the 1:2 Np(V) complexes with OX, ODA and IDA. In the 1:2 Np(V)/OX complex, the position of the 5f ? 5f transition further shifts to longer wavelengths but the intensity remains similar to that of $NpO_2(H_2O)_5{}^+$ and the 1:1 Np(V)/OX complex. Such observation suggests that the 1:2 Np(V)/OX complex is $NpO_2(OX)_2(H_2O)^-$, with a coordination number of 5 in the equatorial plane without an inversion center. In the 1:2 Np(V) complex with ODA, the absorption band of $NpO_2(H_2O)_5{}^+$ at 980 nm completely disappears, suggesting that the complex is probably $NpO_2(ODA)_2{}^-$, with two tridentate ODA ligands in the equatorial plane. This complex has an inversion center, making the 5f ? 5f transition forbidden. For the 1:2 Np(V)/IDA complex, the absorption band still shows, but the intensity is lower than that of $NpO_2(H_2O)_5{}^+$ and the 1:1 Np(V)/IDA complex. Implications of the band position and intensity on the structure of the complex are discussed. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098 at the Lawrence Berkeley National Laboratory.

JJ5.18

Trivalent Cm speciation in solution. S. Skanthakumar, Mark R. Antonio and L. Soderholm; Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

A detailed understanding of actinide-ion speciation is important for predicting their solubilities and stabilities in aqueous solution. Confirmation of coordination numbers and bonding distances have historically been difficult to ascertain in solution. X-ray absorption studies (XANES and EXAFS) have been successfully used to determine bonding distances, but information about coordination numbers is often of insufficient precision to adequately understand speciation. The recent availability of third generation synchrotrons has allowed the application of high-energy x-ray scattering (HEXS) to questions of solution speciation. The Fourier transform of scattering data obtained from solutions using x-rays with energies greater than 60 keV can be used to determine coordination environments of heavy ions in solution out to the third coordination sphere or higher. The combination of EXAFS and HEXS provides a particularly powerful means of ascertaining details of solution speciation by combining the strengths of both techniques. EXAFS, a single-ion probe, is able to obtain information from dilute or multiphase samples, whereas HEXS can determine coordination numbers with an error of 0.1 in favorable conditions, as well as metrical information about more distant coordination spheres. We have determined the coordination environment of trivalent Cm using a combination of EXAFS and HEXS as a demonstration of the added information obtainable from a combination of these two techniques. The detailed understanding about the Cm coordination number and bonding distances will be presented. This work is supported by the U.S. DOE, OBES, Chemical Sciences under contract W-31-109-ENG-38. The Advanced Photon Source at ANL is supported by the U.S. DOE, OBES, Materials Sciences under the same contract number.

JJ5.19

Metal ion transport through geologic media. L. Soderholm[1,2], Zachary D. Alexander[1], Amanda L. Kilinskis[1], James C. Sullivan[1] and Karrie-Ann Kubatko[2]; [1]Chemistry Division, Argonne National Laboratory, Argonne, Illinois; [2]Civil Engineering and Geological Sciences, University of Notre Dame, South Bend, Indiana.

Understanding heavy-metals speciation in aqueous solution is an important first step in predicting their fate and transport in the geosphere. The oxidation state and coordination environment of dissolved metal ions, including their number and bond distances in the first coordination sphere, constitute the metrical information necessary for a predictive understanding of its solution behavior. In addition, information about correlations at distances longer that those found for the first coordination sphere is necessary for understanding the behavior of an ion under environmentally germane conditions. Specifically, any significant ion-pair formation, dimerization or oligomerization can significantly impact the interaction of a metal ion with geologic media. As part of a study of actinide mobility in the environment, we have considered other metals that are thought to complex with f ions and affect their chemistry. We present studies on Cd, Hg, and Pb interactions with characterized soil samples as a background for future studies on their combined interactions in solutions containing actinide ions, notably uranium and neptunium. This work is supported by the U.S. DOE, OBES, Chemical Sciences and EMSI Program at ANL (W-31-109-ENG-38) and the National Science Foundation through an EMSI grant (EAR02-21966).

JJ5.20

Formation of Uranium Mononitride by the Carbothermic Synthesis. Geunsik Lim and Ronald Baney; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Nitrides was ranked at the top of the list as fast breeder reactor fuels, in part because of their high thermal conductivity, high melting point and high metal atom density; however, they have been difficult to prepare and fabricate. In this study, Uranium mononitride was synthesized by the carbothermic reduction of the mixed oxide in N2 and H2 atmosphere. This synthesis was followed by thermogravimetry (TG) and the products were characterized by X-ray powder diffraction (XRD). The weight change was divided into two parts; i.e. weight loss due to carbothermic reduction of UO2 and weight loss due to removal of carbon by hydrogen. The lattice parameter of the oxide-free sample was 0.4945 nm, and that of the nitride with oxides was 0.4978 nm. The larger lattice parameter of the latter sample is considered to be due to the oxygen dissolved in the nitride. In this method, the rate of the removal of carbon by hydrogen determines that of the formation of high purity UN.With the understanding of the UN synthesis, the fabrication problems of Uranium Nitrides are discussed.

JJ5.21

Preparations of Nanocrystalline Plutonium and Mixed-Metal Plutonium Oxides. Lanee Snow, Edgar Buck and Bruce McNamara; Pacific Northwest Laboratory, Richland, Washington.

With the goal of preparing monodisperse nanocrystals of plutonium oxide and mixed metal-plutonium oxides, we have pursued recent literature synthetic methods for preparation of similar nanocrystalline metal oxides. These approaches use a surfactant or organic chelator to bind the metal and this templates its thermal decomposition to the metal oxide. In general, the surfactant to aqueous/organic solvent ratio, the total volume of the precursor solution and the upper temperature at which thermal decomposition of the precursor solution occurs each appear to critically affect the size and shape characteristics of the final oxide product. Our initial attempts have prepared high surface area Ce, Zr, and Ce/Zr materials with BET surface areas of 30 -90 m^2/g, however the materials were polydisperse and the latter material varied in composition as well. We will present the thermal decomposition pathway of the plutonium precursor materials by thermal gravimetric/ infrared analysis and characterization data on the final oxide materials by TEM (FEI-Tecnai 30s) with EDS analysis, and BET surface area measurements.

JJ5.22

An Ab Initio Study of Atomic Oxygen Adsorption on the (100) Surface of Gamma-Uranium. Pratik P. Dholabhai and Asok Kumar Ray; Physics, University of Texas at Arlington, Arlington, Texas.

Uranium (U), the heaviest naturally occurring actinide element, is located in the middle of the early part of the actinide series, with three 5f electrons hybridizing with the 6d and 7s electrons and demonstrating itinerant behavior. The high-temperature g(bcc) phase can be stabilized at room temperature with the addition of certain impurities. The unusual aspects of the electronic bonding and structures in bulk uranium are apt to be enhanced at a surface or in a thin layer of uranium adsorbed on a substrate, due to the reduced atomic coordination of a surface atom and the narrow bandwidth of the surface states. For this reason, uranium surfaces and films and adsorptions on such may provide a valuable source of information about the bonding in uranium. The uranium-oxygen system is one of the most complex metal oxide systems due to the high reactivity of U with oxygen and oxygen containing systems. In this talk, we will present results on oxygen adsorption on (100) surface of ?-uranium at both non-spin-polarized and spin-polarized levels using the generalized gradient approximation of density functional theory. All calculations have been carried out using the DMol3 suite of programs. For oxygen, a double numerical basis set with polarization functions (DNP) and for U, the outer 14 electrons are treated as valence electrons and the remaining 78 electrons are treated as core with a hardness conserving semi-local pseudopotential. The (100) surface was modeled with three layers of uranium at the experimental lattice constant and the unit cell per layer contains four uranium atoms. To simulate periodic boundary conditions, a vacuum layer of 30A was added to the unit cell of the layers. Oxygen atom, one per unit cell, was allowed to approach the uranium surface along four different symmetrical approaches: i) directly on top of a U atom (top position); ii) on the middle of two nearest neighbor U atoms (bridge position); iii) in the center of the smallest unit structures of the surfaces (center position); iv) inside the U layers (interstitial position). For oxygen adsorption, the bridge position of (100) surface is found to be most favorable site with chemisorption energies of 7.887eV and 7.965eV at the non-spin-polarized and the spin-polarized cases, respectively. The distances of the oxygen adatom from the U surface are found to be 1.19A and 1.22A for the two cases. The magnetic moment for this most favorable site is found to be 0.167?B per atom. Density of states studies indicate very weak hybridization between uranium 5f and oxygen 2p orbitals. Mulliken spin and charge distribution analysis indicates that the interaction of oxygen with the uranium surface takes place primarily in the first layer. This work is supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U. S. Department of Energy (Grant No. DE-FG02-03ER15409) and the Welch Foundation, Houston, Texas (Grant No. Y-1525).

SESSION JJ6: High Pressure

Chairs: Matthias Graf and Richard Haire
Wednesday Morning, November 30, 2005
Independence E (Sheraton)

8:30 AM *JJ6.1

Structural Investigation of -stabilized Plutonium Alloys and Americium Under Pressure and Temperature. Philippe Faure[1], Vincent Klosek[1], C. Genestier[1], Nathalie Baclet[1], Steve Heathman[2], Peter Normile[2], Jean-Christophe Griveau[2], Franck Wastin[2] and Richard Haire[3]; [1]CEA - Valduc, Is Sur Tille, France; [2]European Commission JRC, Institute for Transuranium Elements, Karlsruhe, Germany; [3]Oak Ridge National Laboratory, CSD, Oak Ridge, Tennessee.

The way 5f electrons localise within the actinide series remains a question of fundamental interest and one of the last challenge for condensed matter physicists. A systematic understanding of the pressure (P) and temperature (T) behavior of lanthanides and actinides is critical for developing theories which predict phase stability in f-electron metals under both normal and extreme conditions. To achieve this goal, experimental results are needed to provide a database to allow the proper condensed matter physics and theoretical models to be developed and certified. But experimental data for actinides under both P and T are lacking because of the difficulties of handling radioactive materials and establishing dedicated devices that can ensure safety concerns. Moreover, synchrotron radiation is essential to obtain the quality of P-T XRD information that is required. However, trends in the sequence of structural transformations have been proposed and relationships between both series of f-elements are being established [1, 2, 3]. Among the actinides, plutonium has a unique position as it lies at the border between the lighter actinides (Pa - Np), having itinerant 5f electrons, and the heavier actinides (Am - Cf), that have localised 5f states. The 5f electrons contribution to the bonding, shown to be very sensitive to pressure, temperature and chemical composition, affects most of the properties of the metals or alloys. We aim at presenting recent results obtained under pressure and temperature, with x-ray diffraction or resistivity measurements, on several -Pu stabilized alloys and americium. New phase diagrams and compressibility properties are shown. References: [1] B. Johansson, *Hyperfine Interactions***128**, 41 (2000). [2] A. Lindbaum *al J. Phys. Condens. Matter.* **15**, 2297-2303 (2003). [3] U. Benedict, *AIP conference proceedings 309 part 1*, ed. S. C. Schmidt 241 (1994).

9:00 AM *JJ6.2

Pressure induced phase transitions in AmCm alloy. Sa Li[1], Rajeev Ahuja[2,3] and Borje Johansson[2,3]; [1]Department of Physics, Virginia Commonwealth University, Richmond, Virginia; [2]Department of Physics, Uppsala University, Uppsala, Sweden; [3]Department of Materials Science, Royal Institute of Technology, Stockholm, Sweden.

We have studied the crystal structure of the AmCm binary alloy under high pressure by means of first-principles self-consistent total-energy calculations using the generalized gradient approximation (GGA) within the density functional theory (DFT). The virtual crystal approximation (VCA) is used for the description of the alloy system. In the present study, we investigated the double hexagonal (P63/mmc) structure, the face centered cubic (Fm3m) structure, the face centered orthorhombic (fddd) structure and the primitive orthorhombic (Pnma) structure for the AmCm alloy. The equilibrium volume, bulk modulus and magnetic moment for all these phases are derived. Our calculated transition pressures are in good agreement with recent experiment performed by Lindbaum et al. [J. Phys.: Condens. Matter 15, S2297 (2003)].

9:30 AM JJ6.3

Density Dependence of the δ-α Transition in Pu-Ga Alloys. Hyunchae Cynn, William J. Evans, Bruce J. Baer, Magnus J. Lipp, Choong-Shik Yoo, Adam Schwartz, Mark Wall, Jessee Welch and Ken Visbeck; University of California, Lawrence Livermore National Laboratory, Livermore, California.

It is important to examine alloying effects on plutonium phase stability to understand mechanical properties of plutonium alloys. It has been discovered that small amount of alloying agents like Al, Ga, Ce, Am, and In can be added to retain metastable δ-Pu structure at ambient conditions [1,2]. It has been experimentally reported that δ-plutonium retained with 2 at. % Al undergoes two phase transformations through an intermediate phase, beta prime to alpha prime below 10 kbar [3]. We have examined compression behavior of two Pu-Ga alloys under pressure to examine the effect of the chemical components at high pressure using a diamond anvil cell at HPCAT (16 ID-B, Advanced Photon Source). We determined a phase transition from delta to alpha-prime plutonium at various pressures below 14 kbar with respect to the amount of alloy component. No b prime phase is identified during compression of Pu-Ga alloys unlike Pu-Al alloy. Intermetallic compounds like Pu3Ga and Pu6Fe were not evidenced in any Pu-Ga alloys examined in this study below 20 kbar. We also determined the volume discontinuity at δ- to α '-Pu phase transition showing a strong Ga concentration dependence. We also noted inhomogeneous Ga composition distribution evidenced from the measured lattice parameters of δ-Pu. Acknowledgments: 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. HPCAT is a collaboration among the Carnegie Institution, Lawrence Livermore National Laboratory, the University of Hawaii, the University of Nevada Las Vegas, and the Carnegie/DOE Alliance. References [1] Goldberg, A. and Massalski, T.B. in Plutonium 1970 and other actinide, 875, AIME, New York, N.Y. (1970) [2] Rechtien, J.J. and Nelson, R.D. Met. Trans. 4, 2755 (1973). [3] Zukas, E.G., Hecker, S.S., Morgan, J.R., Pereyra, R.A., Pressure-induced transformation in a Pu-2.0 at. % Al alloy, Proceedings of an International Conference on solid-solid phase transformations, AIME, 1333.

9:45 AM JJ6.4

Resonance Inelastic X-ray Scattering across the Volume-Collapse Transition in Gd metal at High Pressure. Brian Maddox[1,2], Choong-Shik Yoo[1], Andy McMahan[1], Warren Pickett[2], Richard Scalettar[2], Michael Hu[3] and Paul Chow[3]; [1]H-Division/PAT-Directorate, Lawrence Livermore National Laboratory, Livermore, California; [2]Physics Department, University of California, Davis, Davis, California; [3]HP-CAT, Advanced Photon Source, Chicago, Illinois.

Gadolinium (Gd) undergoes a series of structural phase transitions under high pressures: hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ dist-fcc $\rightarrow$ bcm. This last transition occurs at 60 GPa with a $\sim$5 % volume collapse. The relatively large volume collapse has been considered to be due to the change in 4f-electron correlations from highly localized f-electrons to itinerant f-electrons. Similar transitions have also observed in other rare-earth metals, exhibiting a systematic decrease of volume collapse as a function of f-occupancy: $\sim$15 % volume collapse in Ce, $\sim$10 % in Pr, and nearly no collapse in Nd, Pm and Sm. In this perspective, the large 5% volume collapse observed in Gd is an exception and, therefore, the exact nature of the transition is not apparent. To remedy this situation, we have investigated the electronic structure of elemental Gd to 113 GPa using Resonant-Inelastic X-ray Scattering (RIXS) performed at the LIII-edge at ID-D at the HP-CAT at the APS. By monitoring the La1 emission as a function of excitation energy we are able to probe the quadrupole 3d-5d and dipole 3d-4f transitions as a function of pressure, effectively giving the same information as M-edge absorption spectroscopy, where changes in the degree of electron correlation should manifest as changes in the relative intensity of the various RIXS peaks. * This work has been supported by the LDRD-04-ERD-020 and PDRP programs at the LLNL, University of California, under the auspices of the U.S. DOE under Contract No. W-7405-ENG-48

10:30 AM *JJ6.5

High Pressure Structural Phase Transformations in Curium, Americium and Berkelium metals. Rajeev Ahuja, Physics Department, Uppsala University, Uppsala, Sweden.

Density-functional electronic structure calculations have been used to investigate the high pressure behavior of curium (Cm), americium (Am) and berkelium (Bk) metals. The phase transitions from fcc to the low symmetry structures are shown to originate from a drastic change in the nature of the electronic structure induced by the elevated pressure. For the low density phases, an orbital polarization correction to the local spin density(LSD) theory was applied. Gradient terms of the electron density were included in the calculation of the exchange/correlation energy and potential, according to the generalized gradient approximation (GGA). Theory compares rather well with recent experimental data which implies that electron correlation effects are reasonably modeled in our orbital polarization scheme. Using the same approach, we have looked in to the elastic constants of AnTe where An = Th, U, Pu, Am and Np. They compare very well with the recent experimental data. In addition, we will also present our results for high pressure structural phase transition in thorium pnictides and chalcogenides. We compare the calculated structural stabilities with experimental data. For most of the compounds LDA gives the correct ground state but it fails in case of ThSe, ThAs and ThSb. If we instead use the GGA, the correct ground state is obtained also for these compunds. At high pressure all the compounds show a NaCl to CsCl phase transition except ThTe and ThBi which are stable in the CsCl structure already at ambient pressure.

11:00 AM *JJ6.6

Theoretical study of protactinium at high pressure. Borje Johansson[1,2], Sa Li[3] and Rajeev Ahuja[1,2]; [1]Department of Physics, Uppsala University, Uppsala, Sweden; [2]Department of Materials Science, Royal Institute of Technology, Stockholm, Sweden; [3]Department of Physics, Virginia Commonwealth University, Richmond, Virginia.

In the actinide series of elements protactinium is the first one with a substantial occupation of the 5f orbitals. Therefore it is of considerable interest to study the electronic structure of this metal over a wide range of volumes. Recently, high pressure experimental investigations of the crystal structure of Pa have been reported. This provides us with an excellent opportunity to test the accuracy of the theoretical modeling for an actinide system with a substantial band-width of its 5f states.

11:30 AM JJ6.7

Pressure-Induced Electronic Phase Transitions in Rare-Earth Metals. Choong-Shik Yoo, Valentin Iota, Brian Maddox, Jae-Hyun Park Klepeis, William Evans and Hyunchae Cynn; H-Division/PAT-Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Unusual phase transitions driven by electron correlation effects occur in many f-electron metals (lanthanides and actinides alike) from localized phases to itinerant phases at high pressures. Some of these transitions are accompanied with large volume collapses as observed across the d(fcc) - a(monoclinic) phase transition in Pu (DV/V$\sim$20%) and the d(fcc) - a(fcc) in Ce ($\sim$15%). The dramatic changes in atomic volumes and crystal structures associated with these transitions signify equally important changes in underlying electronic structures of these highly correlated f-electron metals. However, the exact nature of these transitions has not been well understood, including the short-range electron correlation effect, its relationship to long-range crystalline order, the possible existence of remnant of the transition in liquid, the role of magnetic moment and order, the critical behavior, among many other issues. Many of these questions represent forefront physics challenges important in understanding the high-pressure behavior of other f- and d-band transition metals and some of their compounds. Therefore, the goal of the present study has been to understand the relationships between the crystal structure, electronic correlation and electronic structure in f-electron metals by using third-generation synchrotron x-ray diffraction and high-resolution x-ray emission/absorption spectroscopy, all applied to the samples in diamond-anvil cells. In this paper, we will describe the pressure-induced structural and spectral changes to 100 GPa in several f-electron rare-earth metals and discuss about the associated changes of electron correlation and crystal structure, governing the volume collapse transitions. * This work has been supported by the LDRD-04-ERD-020 and PDRP programs at the LLNL, University of California, under the auspices of the U.S. DOE under Contract No. W-7405-ENG-48

11:45 AM JJ6.8

Ferromagnetic Interactions in Compressed Transition Metals. Valentin Iota[1], Choong-Shik Yoo[1], Jonathan Lang[2], Daniel Haskel[2] and George Srajer[2]; [1]Lawrence Livermore National Laboratory, Livermore, California; [2]XOR, Advanced Photon Source, Argonne, Illinois.

The electronic and spin interactions in magnetic transition metals are greatly influenced by the spatial arrangement of the atoms in their solid phases. By altering the interatomic distances and potentials, applied hydrostatic pressure affects the band structure, the polarization of the valence band (local spin moment) and the long range magnetic coupling (ferromagnetism). This effect is especially important in the magnetic 3d transition metals (iron, cobalt and nickel), whose phase diagrams reflect a fine balance between configurational and magnetic contributions to the total energy. In these correlated 3d electron systems, pressure induced changes in magnetic moment and electronic structure may influence the phase stability and the crystal structure. In this paper, we report systematic measurements of total magnetic moments in Group VIII 3d-transition metals (Fe, Co, Ni) under pressure as determined by K-edge X-ray near-edge absorption (XANES) and magnetic circular dichroism (XMCD) in diamond anvil cells. Our XMCD results indicate a systematic decrease of ferromagnetic interactions with applied pressure in all three systems studied. In iron, the XMCD signal vanishes sharply upon the structural bcc to hcp transition (12-15GPa), indicating a concurrent magnetic transition to a non-ferromagnetic hcp-Fe. On the other hand, while we measure a clear decrease with pressure in the XMCD of cobalt and nickel, both metals remain ferromagnetic up to pressures well above 100GPa. Further analysis of XANES data indicates that pressure-induced increases in 3d-4p hybridization and bandwidths, lead to diminished spin polarization in the valence band and to the observed reduction in magnetic interactions. This work 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.

SESSION JJ7: Actinide Chemistry I

Chairs: Peter Burns and Jeffrey Hay
Wednesday Afternoon, November 30, 2005
Independence E (Sheraton)

1:30 PM *JJ7.1

Nuclear Waste Forms for Actinides. Rodney C. Ewing, Geological Sciences, University of Michigan, Ann Arbor, Michigan.

Plutonium has been produced in significant enough quantities that it is a source of energy in fission reactions, a source of fissile material for nuclear weapons, and of environmental concern because of its long-half life (Pu-239 is 24,100 years) and radiotoxicity. During the past fifty years, over 1,800 metric tonnes of plutonium and substantial quantities of the 'minor' actinides, Np, Am and Cm, have been generated in nuclear reactors. There are two basic strategies for the disposition of these transuranium elements: 1.) to 'burn' or transmute the actinides using nuclear reactors or accelerators; 2.) to 'sequester' the actinides in chemically durable, radiation-resistant materials that are suitable for geologic disposal. Primary candidates for the immobilization of actinides include silicates (e.g., zircon), phosphates (e.g.,monazite and apatite) and oxides (e.g., zirconolite and muratiate). Recently, there has been substantial interest in the use of isometric pyrochlore, A2B2O7, for the immobilization of actinides, particularly plutonium. Systematic studies of rare-earth actinides in which the B-site may be occupied by Ti, Zr, Sn or Hf, have lead to the discovery that certain compositions (Zr, Hf) are stable to very high doses of alpha-decay event damage. The radiation stability of these compositions is closely related to the structural distortions that occur for specific pyrochlore compositions and the electronic structure of the B-site cation. The type of bonding and the cation electronic structure cause polyhedral distortion and structural deviation from the ideal fluorite structure. These structural changes affect the dynamic defect recovery process and are directly linked to the material's response to and recovery from irradiation. This understanding provides the basis for designing materials for the safe, long-term immobilization and sequestration of actinides.

2:00 PM JJ7.2

Characterization of Actinides during HEDPA Leaching for Aluminum Dissolution in Tank Waste Sludges. Brian A. Powell[1], Linfeng Rao[1], Kenneth L. Nash[2] and Leigh Martin[2]; [1]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Chemistry, Washington State University, Pullman, Washington.

The nuclear waste sludges in underground tanks at Hanford contain most of the actinides as well as non-radioactive materials. Among these materials, aluminum oxide is particularly problematic to the vitrification of high-level waste sludges because it is present in large amounts and it is not as easily removed from the sludge by baseline leaching processes as expected. Besides, interactions of actinides with aluminum oxide have significant implications in designing the strategies for sludge leaching. The objective of this study is to examine the behavior of actinides in the leaching of aluminum oxide with 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), a complexant that forms strong complexes with actinides and aluminum in acidic to basic solutions. Batch adsorption/dissolution experiments were conducted to examine the interactions between lanthanides/actinides and the aluminum oxyhydroxide boehmite (γ-AlOOH) in 1.0M NaCl solutions containing HEDPA. In the pH range 4 to 9, complexation of aluminum by HEDPA significantly enhanced dissolution of boehmite. This phenomenon was especially pronounced in the neutral pH region where the solubility of aluminum is limited by the formation of sparsely soluble aluminum hydroxides. At high pH levels, dissolution of boehmite is inhibited by HEDPA. Systems without HEPDA present exhibited higher concentrations of aluminum in the aqueous phase than those with HEPDA. Both enhancement and inhibition of boehmite dissolution are assumed to be due to differing modes of coordination between HEDPA and the boehmite surface. Data are discussed in terms of the complexation of aluminum and lanthanides/actinides with HEDPA and the effect of complexation on leaching of the lanthanides/actinides from the boehmite surface. The results of the leaching of lanthanides/actinides from aluminum (oxyhydr)oxides by HEDPA (and simultaneous dissolution of the aluminum solid) are of significant importance to the development of pretreatment processes for nuclear waste sludges. This work was supported by the Director, Office of Science, Office of Biological and Environmental Research of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098 at the Lawrence Berkeley National Laboratory.

2:15 PM JJ7.3

Gas Generation from Water Adsorbed Onto Pure Plutonium Dioxide Powder. Kirk Veirs, Laura Worl, John M. Berg, David Harradine, Max A. Martinez and Adam R. Montoya; Nuclear Materials Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Storage and transportation of plutonium dioxide powder is becoming more common due to the disassembly of weapons, reprocessing of nuclear fuel (not in US), and studies to support disposition of plutonium in MOX fuel. Plutonium dioxide powder is a thermodynamically stable ceramic at normal storage or transportation temperatures, and, as such, is an ideal storage form. However, plutonium dioxide powder adsorbs water from the atmosphere with the amount of adsorbed water dependent upon the specific surface area of the powder and the relative humidity.1 DOE's 3013 Standard for fifty-year storage of plutonium materials requires a sealed container.2 The results of a recent study suggest the possibility of producing flammable or detonable gas mixtures from the radiolysis of sorbed water when plutonium dioxide with small amounts of water is stored in a sealed container.3 Gamma radiolysis studies of water on similar oxides show a dramatic increase in the hydrogen G-value to between 5 and 150 molecules of H2 per 100 eV as the water content decreases and the number of water layers approaches a monolayer.4 In contrast, our results of hydrogen generation from pure plutonium dioxide powders with water content more representative of packaged materials indicate a much lower hydrogen G-value by orders of magnitude and no observable production of oxygen. The relationships between specific surface area, water content, number of monolayers of water, and the production of hydrogen and oxygen from radiolysis of water sorbed onto plutonium dioxide powder will be discussed. 1. Paffett M. T., Kelly D., Joyce S. A., Morris J., Veirs K., "A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces", J. Nuc. Mat., 322, 45-56 (2003). 2. DOE-STD-3013-2000, "Stabilization, packaging, and storage of plutonium-bearing materials", U.S. Department of Energy, Washington, D.C.. 3. M. V. Vladimirova, I. A. Kulikov, "Formation of H2 and O2 in Radiolysis of Water Sorbed on PuO2", Radiochemistry 44, 86-90 (2002) 4. J. A. LaVerne and L. Tandon, "H2 Production in the Radiolysis of Water on CeO2 and ZrO2", J. Phys. Chem. B 2002, 106, 380-386.

3:30 PM *JJ7.4

Mechanisms of Long-Term Uranium Transport under Oxidizing Conditions. Takashi Murakami, Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan.

Understandings of U transport at the Earth's surface are quite important especially for the disposal of radioactive waste and the remediation of contaminated ground water. Uranium(IV) is unstable under oxidizing conditions and oxidized to U(VI) that is soluble. The mobility of U(VI) is controlled by mineral-water interactions, and U adsorption to clays and clay minerals has been believed to be a dominant mechanism to control U transport. We examined U transport in the weathered zone of the Koongarra U deposit, Australia, which has been subjected to weathering for the past 2 million years. The ground waters are undersaturated with respect to uranyl minerals. The highest U concentration in the ground waters of the ore area was about 400 ppb but the U concentration decreased to 0.2 ppb in a creek, 200 m downstream the ore. To clarify the U immobilization mechanisms in this zone is a key for understandings of the mechanisms of long-term U transport. For about 100 ppb U (10(-7) mol/L) ground water, the formation of saleeite [Mg(UO2)2(PO4)2.10H2O] occurred at the rim of apatite [Ca5(PO4)3(F,OH)] by local saturation. To understand the mechanism of the saleeite formation, we carried out a laboratory experiment where apatite was reacted with U-containing solution and the product solution was undersaturated with respect to uranyl phosphate minerals. Autunite [Ca(UO2)2(PO4)2.10H2O] was formed at the rim of apatite like in the field. Note that there was not Mg in either mineral or solution. Rutherford backscattering spectrometry revealed that a leached layer of tens of nanometer thick was formed on dissolving apatite, autunite was precipitated only in the leached layer by local saturation, and autunite precipitated was added to the interface between the leached layer and solution. This is the mechanism of the autunite formation at the rim of apatite, and the mechanism of U immobilization in Koongarra. For about 10 ppb U (10(-8) mol/L) ground water, U occurred as nanocrystals (20-100 nm in size) of uranyl phosphates such as metatorbernite [Cu(UO2)2(PO4)2.8H2O], scattered between and attached firmly to nanocrystals (2-50 nm in size) of goethite and hematite as revealed by high-resolution electron microscopy. Uranium, P, and Mg or Cu adsorbed onto ferrihydrite form nanocrystals of uranyl phosphates during crystallization of goethite and hematite from ferrihydrite. We conclude that the above two mechanisms of U mineralization lower the U concentration in ground water at Koongarra.

4:00 PM JJ7.5

Oxygen Exchange and Diffusion in Uranium Dioxide Single Crystals. Stephen Joyce[1], Mark Paffett[1] and Jeffrey Stultz[1,2]; [1]Los Alamos National Laboratory, Los Alamos, New Mexico; [2]US Borax, Boron, California.

There are a number of solid uranium oxides ranging from U(II)O to U(VI)O$_3$, with essentially a continuous range of stoichiometries from UO$_{2-x}$ up to UO$_3$. UO$_2$ is fairly stable under normal ambient conditions and is the form often used in oxide fuels and in many waste forms. There are concerns related to changes in the chemical and mechanical properties of the UO$_2$ upon bulk oxidation. Bulk oxidation proceeds by at least two steps: 1) oxygen incorporation into surface and 2) subsequent diffusion into the bulk. We have examined both steps using water adsorption on single crystal UO$_2$. In the first set of experiments, a U^{16}O$_2$ sample is exposed ^{18}O-labeled water and investigated using electron stimulated desorption (ESD). In ESD, electron irradiation leads to the desorption of oxygen ions from the surface layer only. For clean UO$_2$ surfaces, only ^{16}O$^+$ is observed; both ^{18}O and ^{16}O are seen for water-exposed surfaces, even at cryogenic temperatures. The exchanged ^{18}O, however, remains at the surface up to temperatures as high as 650K, above which it decreases due to diffusion into the bulk. In the second set of experiments, a UO2 surface is made oxygen deficient by ion sputtering. This reduced surface is reactive to water leading to H$_2$ desorption at 400K. By annealing the sample to various temperatures prior water exposure, we find the surface reoxidizes by diffusion of oxygen out of the bulk at $\sim$700K. From these studies, we can determine the diffusion constant of oxygen in UO$_2$ at 700K. The calculated D ($\sim 10^{-17}$ cm^2/sec) is in good agreement with extrapolations from previous high temperature (>1200K) studies.

4:15 PM JJ7.6

The optical properties of a polished uranium surface and its epitaxial oxide, and the rate of oxide growth determined by spectrophotometry. Wigbert J. Siekhaus, Dept of Materials Science and Chemistry, Lawrence Livermore National Laboratory, Livermore, California.

Wide-band (190-900 nm) spectrophotometry combined with spectral analysis that incorporates the Forouhi-Bloomer dispersion equations for n and k [Forouhi and Bloomer, Phys. Rev. B 34, 7018 (1996); 38, 1865 (1998)] was used[1] to determine the optical properties of freshly polished uranium and of the epitaxial oxide layer as well as the rate of growth of the oxide in air. Optical properties of the oxide change with growing oxide thickness, as is also observed in diffuse reflectance infrared spectroscopy. Results for uranium metal as well as for epitaxial oxide are compared with single wavelength ellipsometry literature values, and n and k for thick epitaxial oxide is compared with values deduced from reflectance values for single crystal UO2 maintained in ultra-high vacuum. 1 Courtesy of n&k Industries, Santa Clara, California 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.

4:30 PM JJ7.7

Morphological Dependence of Oxidation Rate in Uranium Films. Peter Morrall[1,2], A. J. Nelson[2], W. Siekhaus[2], W. McLean[2], P. Roussel[1] and D. Geeson[1]; [1]AWE, Reading, Berkshire, United Kingdom; [2]Lawrence Livermore National Laboratory, Livermore, California.

Spectroscopic ellipsometry has been employed to investigate the optical properties and oxidation rate of a polished polycrystalline uranium sample and sputter deposited films of uranium. The sputter deposited films were grown to an approximate thickness of 1 micron on sputter cleaned silicon wafers having a 100 Angstrom titanium adhesion layer. The growth pressure was varied to obtain uranium films with differing density and porosity. Secondary electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoemission spectroscopy (XPS) measurements were collected from the polished uranium and sputter deposited films in order to assist in determining the morphology, the surface composition, and the uranium oxidation state. Furthermore, since literature data is scarce in relation to the optical properties of uranium and uranium oxide in the visible region, this research has provided increased understanding of these properties through modelling of the spectroscopic data obtained during oxidation. The differences in oxidation behaviour of these films are discussed in the context of the differing morphology and optical properties of the underlying uranium metal substrates.

4:45 PM JJ7.8

Oscillatory Extraction − New Method of F − Elements Separation. Mikhail Alexander Afonin, Alexey Alekseevich Kopyrin, Andrey Aleksandrovich Fomichev and Mussa Ekzekov; Rare Earth, SPIT, Saint-Petersburg, Russian Federation.

The new separation extraction method was created based on oscillatory extraction/stripping process in two extractors coupled by bulk liquid membrane. The experimental setup to investigate the kinetics of non-stationary processes was built in Saint Petersburg state institute of technology at Rare Earth department. This setup could be used to separate macro-concentration of similar elements or isotopes as well. The setup consists of two extractors coupled by liquid membrane (tributyl phosphate in hydrocarbon). Separation of aqueous and organic phases is carried out in centrifugal separators EC-33 (NIKIMT, Russia). Temporal dependence of absorbance spectra of all phases is registering using flow-through cells. Four spectrophotometers (PMR-11 and SF-2000) on the basis of CCD array provides the registration of all phases spectra captured during 0.1-4.0 sec in wavelength range from 200 to 1100 nm every 4.5− 15 sec. Emulsion turbidity is controlled by turbidimeter Orbeco-Hellige Model 966 (Kernco). The parameters of extraction system: pH, red/ox potential of aqua phase, temperature and emulsion turbidity are displayed immediately on a graph and recorded to the computer with frequency above 1 Hz using specially designed software. The software for automation of the setup devices calibration, controlling of the process during the experiment and for experiment results processing is developed. To induce the oscillatory extraction-stripping process the cyclic Belousov-Zhabotinsky (BZ) reaction or cyclic electrochemical oxidation-reduction was used. It is shown the possibility to use oscillatory extraction approach to separate similar elements by using the differences in their kinetic properties. The experimental evidences of uranium, cerium and neodymium isotopes separation were obtained. It shown that the separation of Rare Earth Elements using oscillatory extraction method is higher than the separation of these elements in the classical extraction systems. The mathematical model of none-stationary oscillatory extraction systems is created. The model results are in good agreement with the experimental results. The possible applying of this new technique to separate similar elements and isotopes from aqueous phases is discussed. Acknowledgements.This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under grant RC0-20000-SC14 and RUC2-20011-ST-04 administered by the Civilian Research and Development Foundation.

SESSION JJ8: Actinide Chemistry II

Chairs: Mark Antonio and John Sarrao
Thursday Morning, December 1, 2005
Independence E (Sheraton)

8:30 AM *JJ8.1

A Walk Across Actinide Iodates from Thorium to Californium. Thomas E. Albrecht-Schmitt[1], Richard E. Sykora[2], Zerihun Assefa[2], Richard G. Haire[2], Amanda C. Bean[3], Wolfgang Runde[3] and Brian L. Scott[3]; [1]Chemistry and Biochemistry, Auburn University, Auburn, Alabama; [2]Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

In this talk we will survey the structures, vibrational and emission spectra, and radiation damage in actinide iodate compounds. We will begin with simple thorium compounds and make our way almost entirely through the bulk of the actinide series including Cf(III) iodate. In transplutonium iodates radiation damage becomes a serious problem; the effects of neutron and alpha self-irradiation will be discussed.

9:00 AM *JJ8.2

Similarities between the coordination of actinide ions in solution and the structures of their related crystalline phases. L. Soderholm[1,2] and S. Skanthakumar[1]; [1]Chemistry Division, Argonne National Laboratory, Argonne, Illinois; [2]Civil Engineering and Geological Sciences, University of Notre Dame, South Bend, Indiana.

High-energy x-ray scattering (HEXS) data from actinide ions in aqueous solution are providing new information about solute coordination environments that will enhance the predictive understanding of their chemical stability, solubility and physical properties. The detailed metrical information about the type and number of coordinating ions in the first and more-distant coordination shells is needed to validate calculations on the energetics of metal solvation. Whereas this information is readily obtainable from x-ray diffraction data on crystalline materials, the correlations in solution are by definition less well defined. EXAFS spectroscopy has been successfully used to provide information on near neighbor correlations but often the results are not precise enough to answer specific questions about the number of coordinating ions and their ligation. The increased precision of coordination numbers determined from HEXS, combined with the observation of correlations out to distances of 8 A, is providing new insights into the atomic structure of solution aggregates and how these structural motifs map onto known crystalline phases. This work is supported by the U.S. DOE; Chemical Sciences and EMSI Program at ANL (W-31-109-ENG-38) and the National Science Foundation through an EMSI grant (EAR02-21966).

9:30 AM JJ8.3

Innovative Synthesis Methods of Mixed Actinides Compounds with Control of the Composition Homogeneity at a Molecular or Nanometric Scale. Stephane Grandjean, Benedicte Chapelet-Arab, Stephane Lemonnier, Anne-Charlotte Robisson and Vigier Nicolas; Nuclear Energy Direction - Radiochemistry and Process Department, CEA, Bagnols-sur-Ceze, France.

Actinides contained in the spent nuclear fuel need to be managed in the future fuel cycles for the sustainability of this source of energy. The major ones such as uranium or plutonium are very valuable for energy production within a new fuel. The minor ones such as neptunium, americium or curium contribute to the long-term radiotoxicity of the nuclear waste if not separated and transmuted within new fuels or dedicated targets. Innovative concepts for future fuels or transmutation targets focus on mixed actinides or mixed actinide-inert element materials. For their synthesis, wet methods fulfill very useful requirements and above all a better accessibility to very homogeneous compounds and interesting nanostructures. When dealing with plutonium or minor actinides, this last characteristic is of great importance in order to avoid the so-called "hot spots" and to limit macroscopic defects in the fuel material. In this communication, experimental results are given to illustrate interesting achievements to control the composition or the structure of mixed actinides compounds at a molecular or at a nanometric scale using co-precipitating techniques or sol-gel methods. The first illustration describes the flexibility of the oxalate ligand to modulate the nanostructure of actinides-based solid precursors and obtain mixed actinides oxide following a thermal treatment of the oxalate precursor. New mixed oxalate structures which present original features such as accepting in the same crystallographic site either a tetravalent actinide or a trivalent one are noticeably detailed. Monocharged cations equilibrate the charge in the 3D structure depending on the molar ratio of trivalent to tetravalent actinides. These oxalate compounds are particularly suitable precursors of oxide solid solutions for various actinides systems. The second illustration deals with the control of inorganic condensation reactions of tri- and tetravalent cations in solution by using suitable ligands with a view to obtaining homogeneous oxy-hydroxyde mixtures. The results obtained using Zr(IV), Y(III) and Am(III) or Nd(III) are quite original: a very stable colloidal sol is obtained at pH 5-6 and a nanostructured mixed oxy-hydroxide phase is formed by adapting the sol-gel transition conditions. The initial interactions between the oxy-hydroxide Zr nanoparticles, the ligand and the trivalent cations at a nanometric scale in the sol give access, after gel formation and thermal treatment, to a crystallized phase (Am-bearing cubic Y-stabilized Zirconia) at comparatively low temperatures. In both cases, the simultaneous co-precipitation or co-gelation of the involved actinides remains a challenge because of the specific properties of each actinide, properties which moreover differ according to various possible oxidation states.

9:45 AM JJ8.4

Theoretical Studies of Hydrogen and Water Adsorption on Actinide Oxide Surfaces. P. Jeffrey Hay, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

The adsorption of H_2O and H_2 on UO_2 and PuO_2 surfaces is studied using density functional theory approaches. Periodic slab models are employed to represent the oxide surface with unit cells typically comprised of 20 to 40 atoms. The structures and binding energies of molecular and dissociated species arising from H_2O and H_2 on the (111), (110) and other relevant oxide surfaces are examined and compared to available experimental information.

10:30 AM *JJ8.5

Occurrence and Significance of Multiple Uranyl Species in Environmental Samples. Richard Reeder, Dept. of Geosciences, SUNY at Stony Brook, Stony Brook, New York.

The wide variety of natural ligands available for complexation with uranyl ion and the variability of coordination in its equatorial plane commonly result in the occurrence of multiple uranyl species in environmental samples, thereby complicating prediction of solubility, retention, and mobility. Formation and persistence of multiple uranyl species may be favored where multiple attachment sites are present at solid surfaces. Different binding preferences may result in heterogeneous sorption and incorporation of different uranyl species from solution. If preferences for binding at different sites contrast greatly, the overall interaction of a dissolved species with the surface may depend strongly on the distribution and availability of favored sites, and consequently may lead to either enhanced or diminished uptake capacity of uranyl species. We describe heterogeneous incorporation of minor uranyl carbonate species at the (104) surface of calcite (CaCO3), the most common growth form of this common mineral phase. EXAFS spectroscopy demonstrates the presence of carbonate ligands coordinating in the equatorial plane, but with subtle differences compared to aqueous uranyl carbonate species. Fits of EXAFS data allow for but do not prove the existence of multiple species. We use luminescence spectroscopy to confirm the presence of multiple uranyl species in bulk samples, and spatially resolved luminescence spectroscopy to demonstrate heterogeneous and preferential incorporation of uranyl species corresponding to the surface distribution of structurally non-equivalent growth steps. Spectral structure from uranyl luminescence at one set of growth steps and featureless, weak luminescence at a nonequivalent set of steps are consistent with averaged spectral features observed in bulk calcite samples. The growth step-selective incorporation of uranyl can be explained by a proposed model in which the allowed orientation for adsorption of the dominant aqueous uranyl carbonate species is controlled by the atomic arrangement at step edges. Differences in the tilt angles of carbonate groups between non-equivalent growth steps favor adsorption of the uranyl carbonate species at the growth steps where it is observed from experiments. The findings demonstrate that heterogeneous surface properties of mineral phases may induce the formation and persistence of multiple species of an actinide. This finding implies that solubility, retention, and potential release behavior of U(VI) and other radionuclides may depend on the detailed coordination of the different species present in the solid sorbent.

11:00 AM *JJ8.6

Complexation of Actinides in Solution at Variable Temperatures: An Integrated Approach of Thermodynamic Measurements and Spectroscopic Characterization. Linfeng Rao, Lawrence Berkeley National Laboratory, Berkeley, California.

Reliable models for predicting the chemical behavior of actinides in aqueous processing and in natural environments must properly take into consideration the temperature effect on the complexation of actinides with ligands that may be present. Currently, the majority of thermodynamic data on the complexation of actinides are obtained at or near 25^{o}C. Very few data are available at elevated temperatures. Approximation methods, including the "constant enthalpy" approach, the "constant heat capacity" approach, the DQUANT equation and the revised HFK equation, have not been extensively tested with actinides because of the lack of experimental data. To extend the thermodynamic database to include the effect of temperature on the complexation of actinides, systematic studies are conducted to investigate the complexation of actinides in solution at variable temperatures. Thermodynamic measurements are conducted using variable-temperature potentiometry, calorimetry and spectrophotometry. Thermodynamic parameters including complex formation constants, enthalpy, entropy and heat capacity of complexation are determined. The thermodynamic data, in conjunction with the structural information obtained by spectroscopic techniques, provide insight into the fundamental nature of actinide complexes and the role that solvents play in the complexation. The approximation methods for predicting the effect of temperature on actinide complexation are tested with the experimental data. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098 at the Lawrence Berkeley National Laboratory

11:30 AM JJ8.7

Speciation of Uranyl Peroxy Carbonates in Basic and Weakly Acidic Carbonate Solutions. Bruce McNamara, Lanee Snow and Judah Friese; Pacific Northwest Laboratory, Richland, Washington.

We have been investigating chemical and temperature dependent perturbations to the known speciation of the actinyl carbonates in the pH region between 5 and 9. Two potentially important ligands that may influence speciation are hydroxide and hydrogen peroxide. Each of these ligands can compete with carbonate as ligand in carbonated water and alter actinide speciation. Hydroxide as ligand is ubiquitous in the environment, while the peroxide ligand will only exist as a ligand near a site that possesses an alpha and/or beta radiation field. Hydrogen peroxide as a ligand forms due to the radiolytic decomposition of water. The predominant, neptunyl, and plutonyl peroxy-carbonates formed in solution above a pH of approximately 8 are thought to be the tri carbonato complexes, whereas below this pH, the dicarbonato species become predominant. In between this range, both species exist. To avoid the complexity of the mixed systems, hydrogen peroxide was added to the actinide tricarbonato species above a pH of 9.6 and also to the dicarbonato species below pH of 5.9. We observed that different peroxide complexes formed in both pH regions. Binding constant data have been measured for some of these and we present results on the characterization of actinyl mixed peroxy-carbonates in solution by ^{17}O, ^{13}C NMR, UV-vis, infrared, and Raman spectroscopy.

11:45 AM JJ8.8

UO_2/H_2O and $Th_{3.9}U_{0.1}(PO_4)_4P_2O_7/H_2O$ interfaces under He^{2+}beam radiolysis: U or Th release and disc alteration. Catherine Myriam Corbel[1], Eric Mendes[1], Thierry Mennecart[2], Claire Tamain[3], Patrick Simon[4], Michel Perdicakis[5], Christophe Jegou[6], Frederic Miserque[7], Ahmet Ozgumus[3] and Nicolas Dacheux[3]; [1]DSM/DRECAM, CEA, Palaiseau, France; [2]CERI, CNRS, Orleans, 45071 , France; [3]IPN, Universite Paris-Sud 11, Orsay, 91 406, France; [4]CRMHT, CNRS, Orleans, 45071 , France; [5]LCMPE, CNRS, Villiers-les-Nancy, 54600, France; [6]DEN/DIEC, CEA, Bagnols-sur-Ceze, 30207, France; [7]DEN/DPC, CEA, Gif sur Yvette, 91191, France.

An approach that has been successful to investigate the properties of irradiated matter has been the use of electron, ion or neutron beams. Such a method is applied here to disc/water interfaces to investigate whether alpha radiolysis needs to be taken into account to predict the interface release and alteration in nuclear industrial applications where the solid is doped with alpha radioactive emitters. The two Air/UO_2/H_2O(Air) and Air/$Th_{3.9}U_{0.1}(PO_4)_4P_2O_7/H_2O$(Air) interfaces considered here are formed with oxides of interest for nuclear waste management. The interfaces are irradiated by the He^{2+}ion beam delivered by the CERI cyclotron (CNRS/Orleans) at fluxes in the range $10^{7-}10^{12}$ He^{2+} cm^{-2} s^{-1}. The beam travels through the gas, the oxide disc and then emerges in deionised water (Millipore 18.2 Mohms) with an energy that varies at the interface between 0 and 10 MeV depending on the disc thickness. ICP_MS is used to determine the U or Th amount in the solutions after acidification. Micro-Raman spectrometry and/or X-ray grazing diffraction are used to determine the crystalline structure of the disc in the near surface region. For UO_2, the electrochemical properties of the interface are also measured in-situ. For UO_2, the U release under irradiation increases strongly. The U release increases continuously as a function of flux. The flux below which irradiation has no longer any effect depends on the U release before irradiation. Evidence is found that the uranium in solution is partly colloidal for high flux irradiation. XRD and micro_Raman give evidence that a uranium peroxide phase, studtite, is formed on the disc. This formation gives evidence that irradiation induces a corrosion process where U(IV) is transformed into U(VI). This is consistent with the electrochemical measurements. The open potential and corrosion current both increase under irradiation. When irradiation is switched off, the open potential decreases sharply and, then, evolves slowly. The corrosion current is lower than under irradiation. For $Th_{3.9}U_{0.1}(PO_4)_4P_2O_7$, the Th and U releases both increases under irradiation. The ratio of the Th to U release deceases as a function of fluence. A new phase is detected on the disc by micro-Raman for a ratio value ≈ 2.5 lower than in the solid. The comparsion bewteen the two interfaces shows that the radiolytic effects are stronger for UO_2than $Th_{3.9}U_{0.1}(PO_4)_4P_2O_7$. Evidence is also gathered that transient radiolytic species control the reactivity of both interfaces under irradiation.

SESSION JJ9: Actinide Chemistry III
Chairs: Heino Nitsche and Lynda Soderholm
Thursday Afternoon, December 1, 2005
Independence E (Sheraton)

1:30 PM *JJ9.1

X Ray Absorption Spectroscopy of Actinides involved in Biological processes,. Christophe Den Auwer[1], Philippe Guilbaud[1], Dominique Guillaumont[1], Mikhail Grigoriev[1,4], Philippe Moisy[1], Claude Vidaud[2], Harald Funke[3], Christoph Hennig[3] and Jean Claude Berthet[5]; [1]DEN/DRCP/SCPS, CEA, Bagnols sur Ceze, France; [2]DSV/DIEP/SBTN, CEA, Bagnols sur Ceze, France; [3]FZR-ESRF, Grenoble, France; [4]IPC Moscou, Moscou, Russian Federation; [5]DSM/DRECAM/SCM, CEA, Gif sur Yvette, France.

General understanding of intramolecular interactions engaged in molecular actinide species, in other words physical chemical mechanisms that drive the affinity of chelating ligands for actinide cations still needs to be deepened. Although these processes have long been undertaken for widely investigated transition metals, far fewer studies have been devoted to complexation mechanisms of actinides by specific chelation sites. As a result, the intramolecular interactions of actinide elements with smart chelates designed for coordination chemistry or bioinorganic chemistry are relatively unknown. In this field, X ray Absorption Spectroscopy has been extensively used as a structural and electronic metal cation probe. Combination with more traditional spectroscopic techniques as spectrophotometry is an ideal tool for the understanding of the chelation mechanism. Metallobiomolecules are considered as elaborate inorganic complexes with well-designed metal active sites. Although the various interaction processes between essential cations to biology and proteins are widely studied, focus on the actinide family is more seldom. Actinide impact to biological cycles has been motivated by risk assessments related to the wide use of nuclear fuel sources and industrial or military applications. In particular, the interaction of these cations with the biologically active complexation sites are only partially understood. The presentation will review some of our recent results on actinide molecular speciation upon complexation by small ligands as aminopolycarboxylic acids or metalloproteins as transferrin.

2:00 PM JJ9.2

The Crystal Structures and Magnetic Properties of Np5+ sulfates. Tori Z. Forbes[1], Peter C. Burns[1,2], L. Soderholm[2,1] and S. Skanthakumar[2]; [1]Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana; [2]Chemistry Division, Argonne National Laboratory, Argonne, Indiana.

Solids containing higher-valence actinides show considerable structural diversity, possess important materials properties, and often significantly impact the mobility of actinides in the environment. Structures are known for about 370 inorganic uranyl compounds (including minerals), and provide the basis for improved understanding of the crystal chemistry of uranium. Much less is known about the chemical behavior and crystal chemistry of neptunium. Neptunium is an important radionuclide for the performance of the proposed geologic repository for nuclear waste at Yucca Mountain due to its long half life (2.14 x 10 6 years) and mobility in groundwater[1]. The ability of Np5+ to complex with anions present in groundwater, in particular carbonate, silicate, phosphate, and sulfate, will be important in determining the fate of Np in the environment[2]. The focus of the current research is to further develop an understanding of the crystal chemistry of Np5+ for compounds with environmentally relevant compositions. Hydrothermal synthesis of Np5+ sulfates has resulted in several new structure types, including infinite chains, sheets and frameworks of neptunyl and sulfate polyhedra. These structures exhibit significant topological departures from those of the uranyl sulfates. Some of these structural differences are associated with cation-cation interactions between neighboring neptunyl ions. Cation-cation interactions are rarely found in U6+ compounds, but are proving to be common in Np5+ structures[3]. Magnetic susceptibility studies of the Np5+ sulfates that exhibit cation-cation interactions indicate ferromagnetic ordering occurs in these materials. [1] R. J. Silva and H. Nitsche, Radiochimica Acta 1995, 70/71, 377-396. [2] K. H. Lieser and U. Muhlenweg, Radiochimica Acta 1988, 43, 27-35. [3] N. N. Krot and M. S. Grigoriev, Russian Chemical Reviews 2004, 73, 89-100.

2:15 PM JJ9.3

Oxidation of uranium nanoparticles produced via pulsed laser ablation. Tom Trelenberg[1], Stephen Glade[2,1], Jim Tobin[1] and Alex Hamza[1]; [1]Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Nuclear Engineering, University of California, Berkeley, California.

Depleted uranium samples were ablated using five nanosecond pulses from a Nd:YAG laser and produced films of $\sim$1600 angstrom thickness that were deposited with an angular distribution typical of a completely thermal ablation. The films remained contiguous for many months in vacuum but blistered due to tensile stress induced in the films several days after being brought into air. While under vacuum (2E-10 Torr base pressure) the films were allowed to oxidize from the residual gases, of which water vapor was found to be the primary oxidizer. During the oxidation the samples were observed with both X-ray and Ultraviolet Photoemission Spectroscopy (XPS and UPS) and were found to oxidize following Langmuir kinetics. That a 2D-surface growth model described the oxidation indicates that, even at these low pressures, oxygen accumulation on the surface is a much faster process than diffusion into the bulk. While bulk diffusion did occur, the oxygen present at the surface saturated the measurements taken using photoemission and diffusion was difficult to observe. A method for determining oxide concentration via photoemission from the valence level, as opposed to the more conventional core levels, is also presented. 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.

2:30 PM JJ9.4

Experimental Measurements of Uranyl Mineral Solubilities at 298K. Drew Gorman-Lewis and Jeremy B. Fein; University of Notre Dame, Notre Dame, Indiana.

The long-term performance of the proposed repository at Yucca Mountain will likely depend on the formation and thermodynamic stability of uranyl minerals. Spent nuclear fuel under conditions present at Yucca Mountain will likely undergo extensive alteration. Consequently, the mobility of U(VI) is a major concern for evaluating the repository performance. The primary control on radionuclide release may be the secondary formation of uranyl minerals; however, the thermodynamic properties and solubilities of a large number of environmentally-important uranyl minerals are unknown. Consequently, this gap in the thermodynamic database for uranyl mineral phases can have significant effects on the ability to generate second- and third-generation Source Term models. We have synthesized rutherfordine, UO_2CO_3; soddyite, $(UO_2)_2SiO_4(H_2O)_2$; and metaschoepite, $(UO_3)(H_2O)_2$; and have conducted reversed solubility experiments as a function of pH. Solubility reversals are crucial for demonstrating equilibrium and for yielding accurate thermodynamic parameters from the experimental measurements, and we control the saturation state of our experimental systems both through pH control as well as by controlling the starting solution compositions. Verification by x-ray diffraction of the identity of the final mineral phase(s) in equilibrium with the aqueous solution confirms the stability of these phases under our experimental conditions. We use the experimental results to determine solubility products and standard state Gibbs free energies of formation for the uranyl phases. These values, in conjunction with previous measurements of the standard enthalpies of formation for rutherfordine and metaschoepite, can be used to calculate the standard state entropies of formation for these two phases and hence the temperature dependence of the solubility products for rutherfordine and metaschoepite. Our results contribute to the creation of a rigorously determined thermodynamic database necessary for evaluating potential repository performance.

3:15 PM *JJ9.5

Nanostructures in Uranium Oxocompounds. Sergey Krivovichev[1,2], Ivan Tananaev[2] and Boris Myasoedov[2]; [1]Crystallography, St.Petersburg State University, St.Petersburg, Russian Federation; [2]Institute of Physical Chemistry RAS, Moscow, Russian Federation.

Within the recent years, considerable research efforts were concentrated on synthesis and investigations of structure and properties of uranium minerals and synthetic compounds. It is of great interest to elaborate experimental techniques of fabrication of nano- and mesostructured materials on the basis of uranium and other actinide oxocompounds. One of the routes to the nanomaterials is exploration of organic/inorganic phase separation and phenomena at the interface between organic and inorganic substructures. We have investigated a series of crystalline and semi-crystalline phases in the uranyl selenate-water system with addition of amines with various shape and structure. As a result, a number of structures were obtained in which complex organic-inorganic substructures are in the nanometer-range size. These include: (1) nanotubular structures consisting of topologically complex uranyl selenate nanotubules [1,2]; (2) structures with highly ordered cylindrical organic micelles inserted into flexible inorganic substructure [3]; (3) lamellar nanocomposite structures with alternating organic and inorganic lamellae. These structures can be considered as model systems for formulation of important concepts related to specificity of topology and interactions at the organic/inorganic interface in nanostructured actinyl oxocompounds. In particular, the concept of charge density matching has to be modified in order to take into account relatively low charge density of the 2D boundary of the inorganic substructure. 1. Krivovichev S.V., Kahlenberg V., Kaindl R., Mersdorf E., Tananaev I.G., Myasoedov B.F. Angew. Chem. Int. Ed. 44, 1134-1136 (2005). 2. Krivovichev S.V., Kahlenberg V., Tananaev I.G., Kaindl R., Mersdorf E., Myasoedov B.F. J. Amer. Chem. Soc., 127, 1072-1073 (2005). 3. Krivovichev S.V., Kahlenberg V., Kaindl R., Mersdorf E. Eur. J. Inorg. Chem. 2005, 1653-1656 (2005).

3:45 PM JJ9.6

Presence and Persistence of Uranyl Peroxide Nanoclusters Upon Dilution and in Contact with Geological Media.

Karrie-Ann Kubatko[1], Peter Burns[1], Lynne Soderholm[2] and Mark Antonio[2]; [1]Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana; [2]Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

Several Mo, W, S and V-based peroxo-bearing clusters are known to form in aqueous solutions in the presence of small quantities of H_2O_2. While studtite is the only mineral known to contain polymerized uranyl peroxide polyhedra, four U-based peroxo-nanoclusters have recently been isolated and structurally characterized. These structures are based on the polymerization of 20, 24, 28 and 32 uranyl polyhedra. Uranyl peroxo-nanoclusters represent a new direction in actinide chemistry and a new class of polyoxometalates. Uranyl peroxides may form in alkaline mixtures of high-level radioactive waste, such as the high-level waste storage tanks at the Hanford site, Washington. Such phases may form by the incorporation of peroxide created by alpha-radiolysis of water. The presence and persistence of such phases could profoundly impact the mobility of actinides in the environment. The potential for uranyl peroxide clusters to exist in dilute aqueous solutions, as well as the significance of such phases in nuclear waste management, provides the impetus for further study of this unusual family of nanoclusters. Three sets of experiments were performed on parent solutions containing the 24-polyhedral nanoclusters. These solutions were (1) diluted using alkaline solutions to maintain a constant pH, (2) diluted in H2O or dilute HCl to alter the pH, and (3) reacted with quartz, plagioclase, biotite, kyanite, kaolinite, and welded tuff. Small-angle X-ray scattering data for representative solutions were collected at the Advance Photon Source at beam line 12-BM-B, Argonne National Laboratory. Data for the ten-fold dilutions (in alkaline solutions, H2O, and in contact with geological media) contains spherically-ripened monodisperse clusters. Uranyl peroxide nanoclusters were present in solutions at near-neutreal pH, as well as dilutions down to 0.001 M uranyl ion. The best fit of the I(Q) vs. Q data from the spectra required a spherical shell model, with an overall cluster diameter of $\sim$16.2 $\mathring{A}$, in excellent agreement with that obtained from the solid-state structural data. Verification of the existence and stability of the 24-polyhedra molecular cluster in dilute solution at near-neutral pH warrants further chemical and structural studies.

4:00 PM JJ9.7

Geochemical approaches to understanding a shallow groundwater flow system in the Kanamaru uranium mineralization area (Japan).

Regis Andre Bros[1], Yoji Seki[1], Atsushi Kamei[2], Yutaka Kanai[1], Koichi Okuzawa[1] and Yoshio Watanabe[1]; [1]Research Center for Deep Geological Environments, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki Prefecture, Japan; [2]Department of Geosciences, Shimane University, Matsue, Shimane Prefecture, Japan.

Groundwater flow investigations in geological systems aim to model past flow patterns over long time-scales (1 Ma or more). These models can be extrapolated to the future, although the current flow system may differ from past states and may not be at equilibrium with present driving forces. Numerical flow simulation are better constrained using geochemical information from both groundwater and bed rocks in addition to hydrogeological data. During a study of the Kanamaru low-grade U mineralization area (Japan), geochemical approaches for understanding a shallow (0-50 m) groundwater flow and related element transport are being assessed. The field of studies is located near a discharge zone and consists of a Cretaceous granodiorite basement overlain by Tertiary fluviatile conglomerates and sandstones. U concentrations up to 320 ppm were identified in mineralized sedimentary layers. 234U/238U (0.8-1.7) and 230Th/234U (0.5-1.8) activity ratios in the mineralized horizon indicate that U remobilization and close redeposition took place within the last 350,000 years. The rate of U lixiviation was sufficiently fast to prevent 230Th from growing back into secular equilibrium with its precursor 234U. U dissolution still continues as indicated by the presence of dissolved U in pore water (0.1-2.5 ppb) and by the good agreement between the concentration of dissolved U and that of the host rock. Deep waters in the granitic basement are Ca- and HCO3-dominated and show slightly acidic to slightly alkaline pH (6.5-7.3) and higher TDS. Shallow waters display lower pH (4.5-6.5). They are more dilute and contain higher Cl content reflecting shallow alteration. Variations of Cl and Br concentrations suggest the existence of Br-rich and Cl-depleted deep groundwater in the basement. Concentrations are in good agreement with hydraulic parameters, i.e. inflow of fresh water and low concentrations in hydraulically conductive fractures. Seasonal variations are also observed in deep groundwater with lower Br concentrations at the end of the dry season. Variations in F concentrations are erratic, possibly reflecting water/rock interactions and groundwater residence time rather than pure mixing alone. Variations of the 87Sr/86Sr ratio indicate the occurrence of two groundwater types: deep waters having low isotopic ratio (0.7090-0.7094) and shallow waters displaying higher ratios (0.7100-0.7107). Reported in a 87Sr/86Sr vs. 1/Sr diagram, the samples plot on a mixing line between two poles: a granitic component (70-80 ppb) and a sedimentary component (10-13 ppb). The data suggest upward migration of low permeable granite-derived Sr through the sedimentary column. This likely occurs by diffusion through permeable sediments therefore competing with the main lateral groundwater flow. The infered minimum distance of upward transfer is nearly 10 m. This case study shows that the present methods can constrain models for fresh groundwater flow and associated mass transfers.

4:15 PM JJ9.8

Phase Composition and Leach Resistance of Actinide-Bearing Murataite Ceramics.

Sergey Stefanovsky[1], Sergey Yudintsev[2], Boris Nikonov[2], Sergey Perevalov[1], Olga Stefanovsky[1] and Alexander Ptashkin[1]; [1]SIA Radon, Moscow, Russian Federation; [2]IGEM RAS, Moscow, Russian Federation.

Phase composition of the murataite-based ceramics containing 10 wt.% ThO2, UO2, NpO2 or PuO2 and leaching of actinides using a MCC-1 procedure were studied. The ceramics were prepared by melting of oxide mixtures in Pt ampoules at $\sim$1500 oC. They are composed of predominant phases of the pyrochlore-murataite series and traces of extra phases (rutile, crichtonite, perovskite). Normally three murataite-related phases with five-, eight-, and three-fold elementary fluorite unit cell were simultaneously observed. In the Th-bearing sample the 5C phase prevails over the 8C phase. In the U-bearing sample they co-exist in comparable amounts. The sample produced at 1500 oC contains crichtonite whereas the ceramic produced at lower temperature (1400 0C) contained rutile. The Np- and Pu-doped ceramics are also composed of major the 5C and 8C phases and minor rutile. Unlike the Pu-sample prepared under slightly reducing conditions the ceramic produced under neutral conditions doesn't contain perovskite-type phase whose occurrence was supposed to be due to reduction of Pu(IV) to Pu(III). Leach rates (7-day MCC-1 test at 90 oC) of the actinide elements from all the ceramics studied are at the level of E-6 to E-7 g/(cm2*day).