SYMPOSIUM JJ
Actinides—Basic Science, Applications, and Technology
November 28 - December 1, 2005

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* Invited paper
SESSION J11: 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 *J11.1

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 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 actinide materials. UCRL-ARS-213005. 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 *J11.2 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 J11.3
Abstract Withdrawn

9:45 AM J11.4 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 Ga concentration 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.


Density-functional electronic calculations have been used to investigate the high-pressure behavior of americium. The phase transition was calculated to coincide 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 in the Am I phase 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 J11.6 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 orbital 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 eigenfunctions as basis. For the bulk calculations, a fcc unit cell with one atom is used. A constant muffin-tin radius (Rmt) of 1.56a.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 Au surfaces 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-FG02-03ER15400) and the Welch Foundation, Houston, Texas (Grant No. Y-1525).

11:15 AM J11.7 First-Principles Calculations of the Properties of Point Defects in Alpha- and Delta-Pu. Babak Sadigh, Jess Steurgone, Per Soderlind and Wilhelm Wolfere; Lawrence Livermore National Laboratory, Livermore, California.

We present extensive first-principles calculations (using spin-polarized density-functional theory within the generalized gradient approximation (DFT-GGA)) 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 J11.8 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 chosen to optimize bulk Pu 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 non-perturbative properties calculations. For the bulk-electron 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 Kmt is determined by Rmt Kmt = 9.0. The Brillouin zone is sampled on a uniform mesh of 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 5.41 and 1.42 J/m^2 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 2.90eV 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).


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. The spin-orbit coupling (SOC) is implemented in the conventional approximate fashion as a perturbation in the full-potential linear muffin-tin orbital method (FPLMT0) whereas in the exact muffin-tin orbital method (EMTO) the exact fully relativistic four component Dirac equation is solved. We showed 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 (FPLMT0) 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 J22: Superconductivity
Chairs: Michael Fluss and James Tobin
Monday Afternoon, November 28, 2005
Independence E (Sheraton)

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 inclusion. 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 of bonding and structural are examined to elucidated trends between compounds.

2:00 PM J22.2 Structural Tuning of PuMgA5, Unconventional Superconductors.
Eric D Hauer1, J. L. Starro1, J. D. Thompson1, L. A. Morales1, F. Wastin2, J. Rebizant2, J. C. Grieu3, P. Javorsky2, P. Boulet2, E. Colineau2, G. H. Lander2 and G. R. Stewart3; 1Los Alamos National Laboratory, Los Alamos, New Mexico; 2European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany; 3Department of Physics, University of Florida, Gainesville, Florida.

The discovery of superconductivity in PuMgA5 (M = Co, Rh) with transition temperatures of Tc = 18.5 K and 8.7 K, respectively, offers a new route by 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 μeff = 0.2μB, close to that expected for a d++(0.8μB) and enhanced electronic specific heat coefficient γ = 100 mJ/mol·K² consistent with moderately heavy fermion behavior. Comparison to the unconventional heavy fermion CeMnB6 (M = Co, Rh, Ir) superconductors reveals contrasting similarity between the two families of superconductors, indicating that structural tuning plays an important role in optimizing superconducting in these materials. Both families of superconductors have a linear variation of Tc with c/a with a nearly identical slope d(ln(Tc))/d(c/a) ~ 100 despite the order of magnitude increase in the transition temperature of the PuMgA5 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 PuMgA5 and CeMnB6 superconductors will be discussed.

3:30 PM J22.3 Superconductivity in the Actinide Systems: Pressure Effect on PuTIGa5 (T=C, Co, Rh) and Americium Metal.

Here we report recent pressure studies on the magnetic and superconducting properties of AnTIGa5 (An=Np, Pu, Am – T=C, Co, Rh, Ir ) and Americium metal down to 0.4 K. Recent discovery of superconductivity in the Plutonium based compounds PuTIGa5 (T=C, Co, Rh) has shed a new light on the study of Actinide compounds. The fact that these systems present a lot of similarities with the CeTIGa5 (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 Tc (△ln(c/a)/△Tc) 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 (Tc~18.5 K for PuCoGa5, and ~0 K for PuRhGa5, and H~2 T and 34 T respectively). Moreover they present at ambient pressure a Non Fermi Liquid described by a T^1/2 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 an 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 Hc(T) under pressure we extract superconducting features of high pressure phases of Americium : this non magnetic element (5f^6, J=3/2,L=0) seems to become Type II superconductor under pressure (Hc1~T at 6 GPa). The complex superconducting diagram Tc(p) related to the several phases transition led us to examine the localization delocalization aspect of the 5f electrons in this metal through the Mott transition.

4:00 PM J22.4 Theory of the Knight Shift and Spin-Lattice Relaxation Rate in Pu-115 Compounds. Yunkyu Bang1, Matthias J. Graf1, Nicholas J. Curro2 and Alexander V. Bahatskyy1; 1Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; 2MST Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

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 rates in PuInCoGa5 by Sautet 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 PuPtCoGa5. It appears that in both Pu-115 compounds superconductivity is mediated by spin fluctuations with similar scaling behavior in the normal state.
What Does the Specific Heat of Actinides at Low Temperatures Reveal? From Pu, Pu, and Am to NbP_{6}\text{Ni}_{2}, PuAl_{2}, and PuGa_{5} to Recent Work on NbCu_{5-\text{Ni}}_{2}, Alloys.

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 $^{239}$U have negligible self-heating and can be measured to below 0.05 K, while those of $^{237}$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 $^{235}$Pu, $^{237}$Np, or $^{243}$Am) may require high sample 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 Nb analog of UCu_{5-\text{Ni}}_{2} 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, 2000
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 $\delta$-Pu 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 across a wide and crystal structure range. The photoemission (PES) data for $\delta$-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 $\alpha$-Pu, PuIn_{3}, PuSb_{2}, $\delta$-Pu, PuSb_{2}, $\alpha$ PuRhGa_{5} 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 temperature 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 $\delta$-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, Adam Schwartz, Per Soderlind, and David Laughlin.

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
Edgar Colin Buck, Rick Wittman and John Abrahall.

State-of-the-art instrumentation for actinide research is often unavailable such as a monochromator electron beam source for TEM that provides an energy resolution of 0.2 eV. In this study, we used a conventional TEM (JEOL 2010) with a LaB_{6} electron source (energy resolution $\sim$0.8 eV at 200 keV) and attached image filter for conducting electron energy-loss spectroscopy (EELS) and used multitelescopic spectral sharpening routines to improve the resolution of EELS features. The main advantage of TEM-EELS over other spectromicroscopic methods, such as XAS or XPS is that the electronic density of states in an extremely small volume of material can be probed. Furthermore, both 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 reached, or achieved near the conventional TEM system. Therefore, 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 correction is 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 actinide solid state. We examined the advantage of running the B-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-PuGa.
Bryndon Chung, Adam J. Schwartz, Bartley E Ellingshaus, Mike J. Fluss, Jeffery J. Haslam, Kerri J. M. Blomma and James G. Tobin.

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 inclusion, and defect clusters. We present here 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 extraatomic 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 and unoccupied 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 macroscopic single crystals of Pu with well-defined surfaces. The talk will include a discussion of resonant photoelectron spectroscopy [1], x-ray absorption spectroscopy [2,3,4], electron energy loss spectroscopy [2,3,4], Fano Effect measurements [5], and bronstein-type isochromat spectroscopy [6], including the utilization of micro-focused beams to probe single-crystal 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, 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, 115109 (October 2003) 2. M. A. Wall, A. J. Schwartz, B. W. Chung, D. K. Shuh, R. K. Schulze, and

11:00 AM JJ3.6 Using Nano-focussed Bremstrahlung Ischemotomography (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 Ischemotomography Spectromicroscopy (nBIS). nBIS 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-focussed 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

Claudia Flinn1

Christophe Den Ayw2, Dominique Guillaumont2, Eric Simon3 and Jerome Roques2,3

DEN/DRCP/SCPS, CEA Marcoule, Bagnols sur Ceze, France; 2Institut de Physique Nucléaire 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 f and d 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 L3 edge (2p→d transition) contains structural information on the coordination polyhedron because of important scattering features. But very little electronic information can be extracted, due to short core hole lifetime, broadening the edge signal. On the other hand, the M4,5 (3d→f transition) and N4,5 (4d→f 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 methods are in molecular compounds, uranium oxides and plutonium will be shown at L3, M4,5 and possibly N4,5 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 bonding properties of the cation with the ligand.

11:30 AM JJ3.8 Temperature Dependence of Phonons and Elastic Constants in Pu and Go-Doped Pu

Denise P. Goia1, S. Y. Hu2 and M. J. Baskes1;1Group T-1, Los Alamos National Lab, Los Alamos, New Mexico; 2Group 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 of 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 in 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. Allen1, Erik Nelson2, Mark Wall3 and Corwin Booth4,5;1Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The local atomic environment and vibrational properties of atoms in monodonic 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 L111-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 192 K for alpha-Pu agrees with our previous measurement of the Pu-Pu-bond in 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 = 45 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 < TCDW can be modeled by the change in bond length distributions resulting from condensation of the CDW. For T > TCDW, the observed Debye temperature of 198 K is in good agreement with other measurements of the Debye temperature for polycrystalline alpha-U.

SESSION J44: Actinide Materials

Chairs: John Joyce and Kevin Moore
Tuesday Afternoon, November 20, 2005
Independence E (Sheraton)

1:30 PM J44.1 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 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 order of approximation given by its cubic elasticity theory for optimally chosen effective elastic constants. For extreme elastic anisotropy, such as for the alkali metals and for \( \delta \)-phase plutonium, analytical solutions or approximation are no longer possible and Green’s Green’s Green’s Green’s Green’s approach are required. The above materials mentioned with extreme elastic anisotropy are also positioned close to the borderline \( C_{12} = C_{44} \) where the elastic Green’s function exhibits a singularity and beyond which the perturbation theory breaks down. Hence, 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 \( \delta \)-phase plutonium on the strain energies for its point defects, for instance, and also for the 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 J14.2
Modeling the Static and Dynamic Aspects of Aging and Radiation Damage in delta-phase Plutonium using Molecular Dynamics Simulations. Alison Kubat1, Wilhelm Georg Wolfe2 and Maria-Jose Caturra2; 1Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Department 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 much qualifying 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 the rms radius 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 US. 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 J14.3
Emerging Magnetism Arising from Self Damage in \( \alpha \) and \( \delta \)-Pu. Scott Finkl, Michael J. Flugence, Davis J. Conard, Min-Chul 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 \( \alpha \)-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 of a time independent form and is governed by some unknown damage function 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 cascades. For our measurements in \( \delta \)-Pu we calculate a diameter of the magnetically affected volume of ~250 Å per damage cascade. This should be compared with an estimated volume that encloses the damage cascade itself (determined from molecular dynamics) of ~100 Å. Hence, the ratio of these volumes is ~<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. A nearly ubiquitous indicator that Pu may be 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.C. Felter, C.A. Krill, S. Finkl, D.J. Conard, M.C. Kubota, T. Diaz de la Rubia, Journal of Alloys and Compounds 368 (2004) pg62-74 [2] F. Rullier-Albenque, H. Alloul, and R. Tourbot, Phys. Rev. Lett., 91(4), 047001, 2003.

3:30 PM J14.4
Thermodynamics of \( \delta-Pu_{1-x}Ga_x \) Alloys and Intermetallics. Theresa Lee, Ubaldo Gallegos, Michael Ramos, Ramiro Perezra, 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 \( \delta \)-phase of Pu and its high temperature solid solution is metastable at room temperature. According to the American Pu-Ga phase diagram, the fcc \( \delta \)-phase of Pu is only metastable at room temperature in this composition range, and the thermodynamically stable state is a two-phase mixture of \( \delta \)-Pu and the intermetallic \( \delta-Pu_{1-x}Ga_x \). We have used high temperature solution calorimetry to determine the enthalpy of formation of \( \delta-Pu_{1-x}Ga_x \) alloy at 25°C. The enthalpy of formation of \( \delta-Pu_{1-x}Ga_x \) alloy with respect to the elements at 25°C, \( \Delta H_f^{\delta-Pu_{1-x}Ga_x} \), can be expressed as

\[
\Delta H_f^{\delta-Pu_{1-x}Ga_x} = (273.4 \times 2 - 405.8x + 8.3)x \text{kJ/mol, } R^2 = 0.99.
\]

A strong negative deviation from ideality indicates that there is a strong thermodynamic driving force for ordering in the fcc \( \delta \)-phase; this is consistent with the x-ray absorption fine structure spectroscopy studies of Cox et. al. The entropy of formation of \( \delta-Pu_{1-x}Ga_x \) and \( c-Pu_{1-x}Ga_x \) at 25°C, \( \Delta H_r^{\delta-Pu_{1-x}Ga_x}(25 \text{°C}) \), is positive between 0.95 and 8.26 at% Ga, suggesting that the \( \delta \)-phase is indeed only metastable, and that the thermodynamically stable state is a two phase mixture of \( \alpha \)-Pu and Pu-Ga alloys, with nearly the same amount of \( \delta \)-phase. The phase diagram is correct can only be found by comparing free energies of formation. Combining our enthalpy of formation data with low temperature specific heat measurements of Taylor et. al., we find that the entropy of formation of \( \delta-Pu_{1-x}Ga_x \) alloy with respect to the elements at 25°C, \( \Delta G_r^{\delta-Pu_{1-x}Ga_x}(25 \text{°C}) \), can be expressed as

\[
\Delta G_r^{\delta-Pu_{1-x}Ga_x}(25 \text{°C}) = (273.4 \times 2 - 420.8x + 3.8)x \text{kJ/mol for } 0.95 < x < 0.0826.
\]

We eagerly await future measurements of the enthalpy, entropy, and free energy of formation of t-Pu\textsubscript{Ga}.

3:45 PM J14.5

Differential scanning calorimetry and dilatometry were used to study the kinetics of the \( \alpha \)-to-\( \beta \) (125°C onset temperature) and \( \beta \)-to-\( \gamma \) (212°C onset temperature) solid-state phase transformations in high purity Pu. DSC analysis clearly shows that upon cooling from above the \( \gamma \)-phase field (>325°C) both the \( \gamma \) and \( \beta \) phases can be retained to room temperature. Phase retention appears to be strongly dependent upon the length of time spent in the \( \gamma \) phase field. The kinetics of the sluggish reversion of these retained phases was measured as a function of time spent in the \( \alpha \), \( \beta \), and \( \gamma \) 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 \( \alpha \), \( \beta \), and \( \gamma \) phase fields will be discussed. LA-UR-05-3947.

4:00 PM J14.6
Evidence of Embryo Formation as a Precursor to the Delta-to-Alpha-Prime Transformation in a Pu-Ga Alloy. Kerri J. M. Blebaum1, Christopher R. Krenn1, Mark A. Wall1, Thaddeus B. Massalski2 and Adam J. Schwartz2; 1Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Department 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 between 375°C and 100°C, between 150°C and 200°C, and between 25°C and 25°C, and that the alpha-prime formed in 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 25°C all showed that alpha-prime formation is less than the 25°C treatments. We hypothesize that embryos of the thermodynamically stable alpha-prim-form or during the conditioning treatments, and that these embryos serve as nucleation sites for alpha-prime upon subsequent cooling. This result is an indication of the non-Billingsley phase diagram. This work was performed under the auspices of the

4:15 PM JJ4.7

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 ~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 Compd. 368 (2004) pp(62-74) and new magnetization studies of radiation damage accumulation and annealing in fcc δ-phase Pu (2.3 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 vacancies 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
Spinal ordering and precipitation in U-6wt%Nb. Luke J. Hsiang and Bikou Zhou; Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California.

Low-temperature ordering 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. Spinal ordering 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 250°C, the transformation sequence is proposed to be supersaturated solid solution α+ -> spinal decomposition -> α (Nb-depleted) + α2 (Nb-enriched) -> ordering transformation and precipitation -> α (ordered) + α2 (ordered) -> α (ordered) + α2 (ordered) -> α (ordered) + α2 (ordered). The precipitation of ordered α2 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
Chair: 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. Blobaum1, Jeremy N. Mitchell2, Christopher R. Krenn3, Mark A. Wall1, Thaddeus B. Massalski2 and Adam J. Schwartz1; 1Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Department of Materials Science and Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania; 3Los Alamos National Laboratory, Los Alamos, New Mexico.

Martensitic transformations can occur via two modes: thermoelastic and burst. In thermoelastic martensites, deformation can be accommodated by small and continuous events that 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 partial 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 deformed alphas may catalyze (or retard) additional transformation. These stress could initiate cascades of alpha-prime particles that revert nearly-simultaneously. The cascades are likely quenched by stress and/or temperature changes required for the transformation. 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 the 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 an aggregate process.

JJ5.2

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 material's face-centered cubic (fcc) 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 + alpha prime. When the metastable delta-phase is cooled into the 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 Chang, Stephen Thompson, Codie Richey 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 helium in-growth and the integrated aging effects will result in microstructural and physical property changes. Because these effects would normally require decades to measure, studies are underway to assess the effects of extended aging on the properties of plutonium containing 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 a cumulative total density by 0.12 to 0.14% and now exhibit a 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.

**J15.4**

**Computer simulation study of self-irradiation effects in plutonium alloys.** Lilian Berlu1, Gaëlle Rosa1, Philippe Faure1 and Gerald Jomard2; 1DRMN/SEMP, CEA, L-sur-Tille, France; 2DPTA/SPMC, CEA, Bruyère le Chatel, France.

The study of self-irradiation effects on plutonium alloys crystallographic structure is of prime importance to determine the time evolution of their physical properties. The α decay of 239-plutonium constitutes 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[3-4]. These primary defects can then diffuse through the crystal, 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 affected 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 method. 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). Further diffusion and recombination process of the defects formed is studied with mesoscopic scale simulations. Here we show recent results obtained by MD calculations. These simulations have been performed using the MEAM interatomic potential formalism[5]. The point defects formation is calculated using a progressive increase in the PKA energy. Further 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) 92-97, L. Filloza, Los Alamos National Laboratory, Los Alamos, New Mexico.

**J15.5**

**Molecular Dynamic Simulations of Phase Stability and Phase Transition Kinetics in Pu-Ga Alloys.** Shenyang Hu, Mike Masks 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 α 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 0 K for Ga, and experimental data at 0 K and elevated temperatures for Pu. Experimental data for the reference phase PuGa (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.

**J15.6**

**Abstract Withdrawn**

**J15.7**

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

Raman spectroscopy can be performed with micrometer resolution and can thus cascade these primary defects 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 nm on wavelength and reflects on 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. This model was compared with the modelled signal 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.

**J15.8**

**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 an 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.

**J15.9**

**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 ultrathin layers by a number of processes which reflect the earth in the EUV imagers 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 portiions 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.

**J15.10**

**Muranite Ceramics Doped with Lanthanides and Uranium.** Sergey Stefanovsky1, Sergey Yudintsev2, Boris Nikonorov2 and Olga Stefanovskaya2; 1StA Radon, Moscow, Russian Federation; 2IGEMRAS, Moscow, Russian Federation.

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

**J15.11**

**Crystal Structure of Uralyl Carboxylates.** Paul Gieting; NASA, J. Porter and Peter C. Burns; Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana.

Uranyl-organic complexation in geochemical fluids can have a profound impact upon uranium solubility and transport. Studies of uranyl-
organometallic crystal structures provide a basis for understanding the complexion of the uranyl ion in solution. Novel uranyl oxalates The crystal structure of novel uranyl oxalate complexes under mild hydrothermal conditions, have been determined. These structures demonstrate new features little or not previously known in this chemical system, in particular polymerization into infinite sheets giving rise to a new linkage of uranyl polyhedra. Further work on the chemistry of this and other systems of hexavanadium uranium and low molecular weight carboxylic acids, especially formic acid, is likely to turn up new insights. Structural classification scheme for uranyl carbocations. 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 amenable to well-coordinated problems such as the environmental transport of hexavanadium uranium as dissolved organic complexes. We offer a simple scheme that classifies uranyl oxalate structures by analyzing the long-range structural features and the solution environment of uranyl ligands, which leads to a structural model 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). U+6+ minerals and inorganic phases: A comparison and hierarchy of crystal structures. The Canadian Mineralogist, 34:845 - 880.

J5.12
Hydrothermal Syntheses, Structures, Ion-Exchange, and Optical Properties of Uranium-Based Materials
Tatiana Y. Shvareva1, James V. Beitz2 and Thones E. Albrecht-Schmitt1; 1Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama; 2Chemistry 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/uranium/lanthanide/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 56Sr from nuclear waste, and second harmonic generation of frequency-doubled light.

J5.13
Polymer Assisted Deposition of Thin Metal Films: A New Technique to the Preparation of Metal Oxides, Metal Nitrides, Redox-Active Metal and Multi-Metallic Films
Piyush Shukla1, Anthony K. Burrell1, T. Mark McCleskey1, Quanxi X. Jia1 and Yuan Lin2; 1Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico; 2Material 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 binder that can be spin coated or dip-coated onto any size or shape substrate. The polymer actively bonds 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 binder is chosen to have a particular 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 easy preparation of multi-metallic films by simply mixing the solutions in the desired stoichiometries. Herein, we report on the preparation of mixed metal oxide, nitride, and reduced metal and multi-metallic systems using the PAD technique.

J5.14
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 11/2-→11/2 intra-4f transition at λ=1.5 μm of optically active rare earths in a broad range of host materials, including dielectrics, ceramics and semiconductors. Data is shown for erbium implanted silica glass, sodalite silicate glass, phosphate glass, Al2O3, Y2O3, Si3N4, LiNbO3, amorphous Si, crystalline Si, and sintered SiO2. The room temperature 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 Laplace 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 host. 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 are the actinides will.

J5.15
Extraction Separation of REE Isotopes in Non-Steady-State Conditions. Alexey Alekseevich Kopyrin1, Mikhail Alexeyevich Afonin1, Alexander Alexelevich Baulin1 and Kenton J. Moody2; 1Rare Earth, SPT, Saint-Petersburg, Saint-Petersburg, Russian Federation; 2Analytical 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 yet. Moreover previous approaches were 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 mostly distributed in the industry (especially in the nuclear 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 235U and 238U 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 tetradeclene). The oscillatory extraction method based on exaggerating the small kinetic differences between isotopes during competitive extraction driven by Bolsovs-Zabotinsky (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 could be 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 appears. The separation of 142Ce and 148Ce 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, $^{148}$Nd, $^{142}$Nd, $^{145}$Nd, and $^{150}$Nd from the light isotope - $^{146}$Nd) in the same experiment factor to the Nd separation of the Nd isotopes in the same experiment. This was accomplished by using a combination of separation techniques. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under grant RCO-20000-SC14 and RUC2-2001-01-ST-04 administered by the Civilian Research and Development Foundation.

**J. J. 16**

Abstract Withdrawn

**J. J. 17**

Optical Absorption, Stability and Structure of NdO$_2$ Complexes with Dicarbonyl Acids. Guozin Tian and Linfeng Ruo; Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California.

Complexation of NdO$_2$ with oxalic acid (O$_2$), oxalyllic acid (O$_2$A), and the inorganic acid (IDA) and this has been studied using spectrophotometry in 1 M NaClO$_4$. Both the position and the intensity of the absorption band of NdO$_2$ at 890 nm are affected by the formation of Nd(V)/dicarbonyl 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 NdO$_2$(V)/TDA complex is quite low (log$eta_{1}$ = 0.88) and comparable to that of NdO$_2$(V)/acetate complex, suggesting only one carbonate group of TDA participates in the complexation. The much higher stability of NdO$_2$(V)/complexes with OX, ODA and IDA indicate that both carbonate groups coordinate with NdO$_2$(V) in these complexes, with possible participation of the ether oxygen in ODA and the nitrogen in IDA. By nature, the absorption band of NdO$_2$ at 890 nm is not sensitive to the transition that is allowed only if the NdO$_2$ species does not have an inversion center. Its intensity is thus sensitive to the equatorial coordination environment of NdO$_2$. It has an intensity of $\sim 35$ M$^{-1}$ cm$^{-1}$ for the free NdO$_2$ species in solution, NdO$_2$(H$_2$O)$_2$. 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 NdO$_2$(H$_2$O)$_2$. On the contrary, the intensity of this transition with ternary complexes is very different from those with OX, ODA and IDA. In the 1:2 NdO$_2$(V)/OX complex, the position of the 5f$^5$ 5f transition further shifts to longer wavelengths but the intensity remains similar to that of NdO$_2$(H$_2$O)$_2$ and the 1:1 NdO$_2$(V)/OX complex. Such observation suggests that the 1:2 NdO$_2$(V)/OX complex is NdO$_2$(O$_2$)(H$_2$O)$_2$ with a coordination number of 5 in the equatorial plane without an inversion center. In the 1:2 NdO$_2$(V)/OX complex with ODA, the absorption band of NdO$_2$(H$_2$O)$_2$ at 880 nm completely disappears, suggesting that the complex is probably NdO$_2$(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 NdO$_2$(V)/IDA complex, the absorption band of intensity is too weak to compare with that of NdO$_2$(H$_2$O)$_2$ and the 1:1 NdO$_2$(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-AC03-76SF00987 at the Lawrence Berkeley National Laboratory.

**J. J. 18**

Trivalent Cm speciation in solution. S. Sastakumara, 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 X-ray adsorption fine structure (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 above the Cm coordination number and bonding distance presented this work was supported by the U.S. DOE, OES, Chemical Sciences under contract W-31-109-ENG-38. The Advanced Photon Source at ANL is supported by the U.S. DOE, OES, Materials Sciences under the same contract number.

**J. J. 19**

Metal ion transport through geologic media. L. Soderholm, Zachary D. Alexander, Amanda L. Kihinski, James C. Sullivan and Kari-Anne Kubatko; 1 Geology Division, Argonne National Laboratory, Arconne, 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 have complex with f ions and affect their chemistry. We present studies on Cd, Hg, and Pb interactions with characterized solid samples as a background for future studies on their combined interactions in solutions containing actide ions, notably uranium and neptunium. This work is supported by the U.S. DOE, OES, Chemical Sciences and EMSI Program at ANL (W-31-109-ENG-38) and the National Science Foundation through an EMSI grant (EAR02-2166).

**J. J. 20**

Formation of Uranium Mononitride by the Carbothermic Synthesis. Gengmeng Li and Ronald Haney; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Nitrides were 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 thermogavimetry (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 oxygen determination by means of the formation of high purity UN. With the understanding of the UN synthesis, the fabrication problems of Uranium Nitrides are discussed.

**J. J. 21**

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

With the goal of preparing monodisperse nanocrystals of plutonium oxide 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 is the total volume of the precursor solution and the 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.

**J. J. 22**

An Ab Initio Study of Atomic Oxygen Adsorption on the (100) Surface of Gamma-Uranium. Pratik P. Dhadihia 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 periodic table of the elements. It has three 5f electrons hybridizing with the 6d and 7s electrons and demonstrating itinerant behavior. The high-temperature (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 U-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 DMolIII 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 hard screening 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 30Å 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 the 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 adsorption energy of 7.887eV and 7.956eV at the non-spin-polarized and the spin-polarized cases, respectively. The distances of the oxygen atom from the U surface are found to be 1.19Å and 1.22Å for the two cases. The magnetic moment for this most favorable site is found to be 0.1077μB 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 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-FG02-03ER15490) and the Welch Foundation, Houston, Texas (Grant No. Y-1525).

SESSION J16: High Pressure
Chairs: Matthias Graf and Richard Haie
Wednesday Morning, November 30, 2005
Independence E (Scheraton)

8:30 AM J16.1 Structural Investigation of stabilized Plutonium Alloys and Americium Under Pressure and Temperature. Philippe Faure1, Vincent Kloes1, C. Genestier1, Nathalie Bacle1, Steve Heathman1, Peter Normile2, Jean-Christophe Griveau2, Frasiz Wastin2 and Richard Haie1, HEC, France; 1European Commission JRC, Institute for Transuranium Elements, Karlsruhe, Germany; 2Oak 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) behaviour 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 the f-electrons and 5f-electrons are established [1, 2]. 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. Johanson, Hyperfine Interactions 128, 41 (2000); [2] A. Lindlbauer et al. J. Phys. Condens. Matter. 15, 2297-2303 (2003); [3] U. Benedict, AIP conference proceedings 500 part 1, ed. S. C. Schmidt 241 (1994).

9:00 AM J16.2 Pressure induced phase transitions in AmCm alloy. Sa Li3, Rajeev Ahuja2,3 and Borje Johansson1,2; 1Department of Physics, Virginia Commonwealth University, Richmond, Virginia; 2Department of Chemistry, Upstate University, College of Arts and Sciences, 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 uniaxial (p(nn)/ymmetric) structure, the face centered cubic (Fm3n) structure, the face centered orthorhombic (Fdd2) structure and the primitive orthorhombic (Pmna) 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 Lindlbauer et al. [1].

9:30 AM J16.3 Density Dependence of the δ-α Transition in Pu-Ga Alloys. Hyoung Gyun Cyan, William J. Egelhoff, James E. Baer, Magnus J. Lipp, Cheong-Shik Yoo, Adam Schwartz, Mark Wall, Jesse 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 at 10 kbar [3]. We have examined compression of the twoPu-Ga alloys under pressure to examine the effect of the chemical pressure 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 PuFe were not evidenced in any Pu-Ga alloys examined in this study below 20 kbar. We also determined the volume discontinuity at δ-α transitions of Pu-Ga phase transition showing a strong Ga concentration dependence. We also noted inhomogeneous Ga composition distribution evidenced from the measured lattice parameters of Pu-Ga. 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 Carnall Institute, 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 actinides, 875, AIME, New York, N.Y. (1970) [2] Rechtein, 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-20 at. % Al alloy, Proceedings of an International Conference on solid-solid phase transformations, AIME, 1333.

9:45 AM J16.4 Resonance Inelastic X-ray Scattering across the Volume-Collapse Transition in Gd at High Pressure. Brian Maddocks1, Choong-Shik Yoo1,3, Andy McMahan1, Warren Pickering2, Richard Scalettar2, Michael Hults3 and Paul Chow2; 1H-Division/PAT-Directorate, Lawrence Livermore National Laboratory, Livermore, California; 2Physics Department, University of California, Davis, Davis, California; 3HP-CAT, Advanced Photon Source, Chicago, Illinois.

Gadolinium (Gd) undergoes a series of structural phase transitions under high pressures: hcp → Sm-type → dhcp → dist-fcc → bccm. This last transition occurs at 60 GPa with a ~5 % volume collapse. The relatively large volume collapse has been considered to be due to the collapse in 4f-electron correlations from highly localized f-electron to itinerant f-electrons. Similar transitions have also been observed in other rare-earth metals, exhibiting a systematic decrease of volume collapse as a function of f-occupancy: ~15 % volume collapse in Ce, ~10 % in Pr, and nearly no collapse in Nd, Sm and Eu. 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 APS. By monitoring the L1 transition as a function of excitation energy, we were able to probe the quadrupole 3d-d and dipole 3d-f 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 *J16.5*

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 compared fairly well with the recent experimental data. In addition, we also will 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 phase ground state but it fails in case of ThS, ThAs and ThSb. If we instead use GGA, the correct ground state is obtained also for these compounds. At high pressure all the compounds show a NaCl to CsCl phase transition except Te and ThBi which are stable in the CsCl structure already at ambient pressure.

11:00 AM *J16.6*

Theoretical study of protactinium at high pressure. Borje Johansson1, Sa Li2 and Rajeev Ahuja1, 2; 1 Department of Physics, Uppsala University, Uppsala, Sweden; 2 Department of Materials Science, Royal Institute of Technology, Stockholm, Sweden;

In the actinide series of elements protactinium is the first one with a substantial band-width of the f-band and 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 *J16.7*

Pressure-Induced Electronic Phase Transitions in Rare-Earth Metals. Chung-Shik Yoo, Valentin Iota, Brian Maddox, Jae-Hyun Park Klepeis, William Evans and Hyunchae Cynn; H-Division/PAT-Director, 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 by large volume collapses as observed across the d(fcc) - (monoclinic) phase transition in Pu (DV/V~20%) and the d(fcc) - a(fcc) in Ce (~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. The goal of 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 relationship 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 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 *J16.8*

Ferromagnetic Interactions in Compressed Transition Metals. Valentin Iota1, Chung-Shik Yoo1, Jonathan Lang2, Daniel Baskel3 and George Srajer2; 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 (12-15 GPa), 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 100 GPa. Further analysis of XANES data reveals that 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 the University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

SESSION J17: Actinide Chemistry I

Chairs: Peter Burns and Jeffrey Hay

Wednesday, November 30, 2005

Independence F (Sheraton)

1:30 PM *J17.1*


Plutonium has been produced in significant enough quantities that it is a source of energy in fission reactors, 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 transuranic elements: 1) to ‘burn’ 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., monazite and apatite) and oxides (e.g., zirconolite and marmorate). Recently, there has been substantial interest in the use of isomeric pyrophore, 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 pyrophore 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 structures provide a 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 J17.2  
Brian A. Powell1, Linfeng Rao1, Kenneth L. Nash1 and Leigh Martin1  
1Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; 2Department 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 because it is present in large amounts and is easily removed during the 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 uranium and plutonium and also the kinetics of actinides leaching 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 oxohydroxide boehmite (γ-AlO(OH)) 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 sparingly soluble aluminum hydroxides. At high pH levels, dissolution of boehmite is inhibited by HEDPA. Systems without HEDPA present exhibited high concentrations of aluminum in the aqueous phase than those with HEDPDA. 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 (oxhydroxides 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, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at the Lawrence Berkeley National Laboratory.

2:15 PM J17.3  
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 unstable ceramic at 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. DOE’s 2013 Standard for fifty-year storage of plutonium materials requires a sealed container. 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.

3:00 PM J17.4  

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 uraninite minerals. The highest U concentration in the ground waters of the ore area was about 450 ppb but the U concentration decreased to 0.2 ppb in a creek. 200 m from the ore. Uranium 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)12.10H2O] 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. Auteinite [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, autinite was precipitated only in the leached layer by local saturation, and autinite precipitated was added to the leachate between the leached layer and solution. This is the mechanism of the autinite 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 metamboethite [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 ferrhydrite form nanocrystals of uranyl phosphates during crystallization of goethite and hematite from ferrhydrite. We conclude that the above two mechanisms of U mineralization lower the U concentration in ground water at Koongarra.

4:00 PM J17.5  
Oxygen Exchange and Diffusion in Uranium Dioxide Single Crystals. Stephen Joyce1, Mark Paffett2 and Jeffrey Stults2  
1Los Alamos National Laboratory, Los Alamos, New Mexico; 2US Borax, Boron, California.

There are a number of solid uranium oxides ranging from U(II) to U(VI)O3 with essentially a continuous range of stoichiometries from UO to UO3. UO is fairly stable under normal surface 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 upon bulk oxidation. Bulk oxidation proceeds by at least two steps: 1) oxygen incorporation into UO and 2) subsequent diffusion into the bulk. We have examined both steps using water adsorption on single crystal UO2. In the first set of experiments, a U18O sample is exposed 18O-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 UO2 surfaces, only 18O is observed; both 18O and 16O are seen for water-exposed surfaces, even at cryogenic temperatures. The exchanged 18O, 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 H2O desorption at 400K. By annealing the sample to various temperatures prior water exposure, we find the surface oxidizes by diffusion of oxygen out of the bulk at ~700K. From these studies, we determine the following constant of oxygen in UO2 at 700K. The calculated D (~10^-17 cm²/s) is in good agreement with extrapolations from previous high temperature (~1200K) good studies.

4:15 PM J17.6  
The optical properties of a polished uranium surface and its epilaxial oxide, and the rate of oxide growth determined by photoacouty. Wigiono J., Jonicka J. A.  
Institute of Physical Chemistry, Warsaw University of Technology, Warsaw, Poland.  
Wide-band (100-900 nm) spectrophotometry combined with spectral analysis which incorporates the Forouhi-Bloomer dispersion equations.
for n and k [Forouhi and Bloomer, Phys. Rev. B 34, 7018 (1996); 38, 1865 (1998)] was used to determine the optical properties of freshly polished uranium and of the epilayer 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 well as observed in diffuse reflectance infrared spectroscopy. Results for uranium metal as well as for epilayer oxidized 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 nkk 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 Morrell1,2, A. J. Nelson3, W. Siekhaus4, W. McLean5, P. Rousell6, and D. Geeson1; 1AWE, Reading, Berkshire, United Kingdom; 2Lawrence 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 Anstrom 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 modeling 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 Alexandrovich Fonichev and Mussa Ekezkov; Rare Earth, SPIT, Saint-Petersburg, Russian Federation.

The new separation extraction method was created based on oscillatory extraction/striping 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 membranes (dextran, phospho in hexagon carbon). 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 (IV-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 960 (Kernco). The parameters of extraction system: pH, red/or potential of aq 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 of 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 showned 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 non-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 RCO-20000-SC14 and RUC2-20011-ST-04 administered by the Civilian Research and Development Foundation.

SESSION J18: Actinide Chemistry II
Chairs: Mark Antonio and John Searro
Thursday Morning, December 1, 2005
Independence E (Sheraton)

8:30 AM *JJ8.1 A Walk Across Actinide Isotopes from Thorium to Californium. Thomas P. Albrecht-Schmitt1, Richard E. Sykora2, Zerihun Assefa2, Richard G. Haire1, Amanda C. Bean3, Wolfgang Runde3 and Brian L. Scott4; 1Chemistry and Biochemistry, Auburn University, Auburn, Alabama; 2Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Chemistry 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 isotopes. We will begin with simple thorium compounds and make our way almost entirely through the bulk of the actinide series including Cf(III) isotope. In transplutonium isotopes 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. Soderholm1 and S. Skanthakumar2; 1Chemistry Division, Argonne National Laboratory, Argonne, Illinois; 2Civil 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 insights into the coordination numbers of 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 number in HEXS, combined with the observation of correlations out to distances of 8 Å, 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 ESMI Program at ANL (W-31-109-ENG-38) and the National Science Foundation through an ESMI grant (EAR02-21966).

9:30 AM JJ8.3 Innovative Synthesis Methods of Mixed Actinide Compounds with Control of the Composition Homogeneity at a Molecular or Nanoscale Level. Stephane Grandjean, Benedicte Chambon-Arab, Stephane Lenoir-Chabot, Andre Nicolas, and Viger 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 radioxicity 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 homogenous 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 actinide-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 complexes in bulk solution. In particular, using Zr(IV), Y(III) and Am(III) or Nd(III) are quite original; a very stable colloid is obtained at pH 5–6 and a nanostructured mixed oxy-hydroxide phase is formed by adding the sol-gel transition conditions. The coordination 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 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 H₂O and H₂ on UO₂ and PuO₂ 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 H₂O and H₂ 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 Uranium Species in Environments. 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 when multiphase systems 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 that solubilize and transport uranyl species with the surface in a heterogeneous manner. Incorporation of uranyl species corresponding to the surface distribution of structurally non-equivalent growth steps. Spectral structure of the uranyl luminescent species on one set of growth steps and featureless, weak luminescence at a nonequivalent set of steps is 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 and 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

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 298°C; these data are adequate for equilibrated 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 experimental data. To expand 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 parameters 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 predict 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-AC03-76SF00098 at the Lawrence Berkeley National Laboratory.

11:45 AM JJ8.8
Speciation of Uranium 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 hydroxide peroxo. Each of these ligands can compete with carbonate to bind with actinyl and 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. Hydroxide peroxo as a ligand forms due to the radiolytic decomposition of water. The predominant, neptunyl, and plutonyl peroxo-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. The competition between these two species can be evaluated by the difference between the range, both species exist. To avoid the complexity of the mixed systems, hydroxide peroxo was added to the actinide tricarbonato species above a pH of 9.6 and also to the dicarbonato species below pH 9.6. We observed that different competition complexes both in pH regions. Binding constant data have been measured for some of these and we present results on the characterization of actinyl mixed peroxo-carbonates in solution by ¹⁷O, ¹³C NMR, UV-vis, infrared, and Raman spectroscopy.

11:45 AM JJ8.9
UO₂/H₂O and Th₁₋₃U₀₋₁(PO₄)ₓP₂O₇/H₂O interfaces under He⁺ beam radiolysis: U or Th release and disc alteration. Catherine Myriam Corbel¹, Eric Meunier¹, Thierry Mennecart², Claire Tamaïn², Patrick Simon², Michel Perdicakis², Christophe Jegou³, Frederic Miserque¹, Ahmed Ouzgounas² and Nicolas Dacheux³, ¹DSM/DRECAM, CEA, Palaiseau, France; ²CERI, CNRS, Orleans, 45071, France; ³IPN, Université Paris-Saclay, 91405, France; ⁴CRHMT, CNRS, Orleans, 45071, France; ⁵LCMP, CNRS, Villiers-les-Nancy, 54600, France; ⁶DEN/DIEC, CEA, Bagnols-sur-Ceze, 30207, France; ⁷DEN/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 (UO₂/H₂O/Air) and Air/Th(Th/sₓPO₄ₓP₂O₇/H₂O/Air) interfaces considered here are formed with oxides of interest for nuclear waste management. The interfaces are irradiated by the He⁺ ion beam delivered by the CERI cyclotron (CNRS/Orleans) at fluences in the range 10⁷–10¹² ions·cm⁻²·s⁻¹. The beam travels through the gas, the oxide disc and then emerges in deionized water (Millipore 18.2 Mohm) 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 release and disc alteration. 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 UO₂, the electrochemical properties of the interfaces are also measured. For UO₂, the U release and 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 colloid for low irradiation. XRD and micro-Raman give evidence that a uranium peroxide phase, studite, 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 decays rapidly and, theoretically, the corrosion current is lower than under irradiation. For Th$_3$UO$_5$$_2$(PO$_4$)$_3$P$_2$O$_7$, the Th and U release both increases under irradiation. The ratio of the Th to U release decreases as a function of fluence. A new phase is detected on the U-rich side [4].

SESSION J9: Actinide Chemistry III

Chairs: Heino Nitsche and Lynda Soderholm
Thursday, December 1, 2005
Independence E (Sheraton)

1:30 PM J9.1
X Ray Absorption Spectroscopy of Actinides involved in Biological processes,. Christoph D. Anver, Philippe Guibaud, Dominique Guillouanton, Mikhail Grigorev, Philippe Moisy, Claude Vidard, Harald Punke, Christof Hennig and Jean Claude Berthet; 1DEN/DRCP/SCPS, CEA, Bagnois sur Cese, France; 2DSV/DIEP/SBTN, CEA, Bagnois sur Cese, France; 3FZR-ESRF, Grenoble, France; 4IPSEM, Moscow, Russia; Russian Federation; DSSM/DRECAM/SCM, CEA, Gif sur Yvette, France.

General understanding of intramolecular interactions engaged in molecular actinide species, in other words physical chemical mechanisms that determine the fate of actinide cations. As a result, the intramolecular interactions of actinide elements with strong 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 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 J9.2
The Crystal Structures and Magnetic Properties of Np$_5^+$ sulfates. Tori Z. Forbes, Peter C. Burns, L. Soderholm and S. Skanthakumar; 1Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana; 2Chemistry 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 uranium compounds (including minerals), and provide the basis for improved understanding of the crystal chemistry of uranium. Much less is known about higher valence and, therefore, the 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 (2,141 x 10 6 years) and mobility in groundwater[1]. The ability of Np$_5^+$ 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 Np$_5^+$ for compounds with environmentally relevant compositions. Hydrothermal synthesis of Np$_5^+$ 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 U(VI) compounds, but are proving to be common in Np$_5^+$ structures[3]. Magnetic susceptibility studies of the Np$_5^+$ 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. Lieder 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 J9.3
Oxidation of uranium nanoparticles produced via pulsed laser ablation. Tom Treleaven; 1Lawrence Livermore National Laboratory, Livermore, California; 2Department 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 ~1000 angstrom thickness that were deposited with an angular distribution typical of a completely thermal ablation. The films remained contiguous for many minutes 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 oxidant. During the oxidation the sample was observed with laser X-ray and Ultraviolet Photoemission Spectroscopy (XPS and UPS) and were found to oxidize following Langmuir kinetics. That a 2D surface growth model was 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 Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

2:30 PM J9.4

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 extreme 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 rutherfordite, UO$_2$CO$_3$; soddyite, (UO$_2$)$_3$SiO$_4$(H$_2$O)$_2$; and metaschoepite, (UO$_4$)(H$_2$O)$_2$; 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 rutherfordite 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 rutherfordite and metaschoepite. Our results contribute to the creation of a rigorously determined thermodynamic database necessary for evaluating potential repository performance.

3:15 PM J9.5
Nanostructures in Uranium Oxo Complexes. Sergey Krivovichev$^{1,2}$, Ivan Tananaev$^2$ and Boris Myasoedov$^2$; 1Crystallography, St. Petersburg State University, St. Petersburg, Russian Federation; 2Institute 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
urnyl selenate-water system with addition of amines with various
shape and structure. As a result, a number of structures were
obtained in which selenate-organic structures in the
nanometer-range size. These include: (1) nanotubular structures
consisting of topologically complex uranyl selenate nanotubes [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 innaturally occurring actinide
complexes.

3:45 PM JJ9:6
Presence and Persistence of Uranyl Peroxo Nanoclusters
Upon Dilution and in Contact with Geological Media.
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Notre Dame, Notre Dame, Indiana; 2Chemistry Division, Argonne
National Laboratory, Argonne, Illinois.

Several Mn, W, S and V-based peroxo-bearing clusters are known to form in aqueous solutions of small quantities of H2O2. While stilbite 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-radioisolation of water. The presence and persistence
of such phases could profoundly impact the mobility of actinides in the
environment. Thus the potential for peroxide clusters uranyl 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. Smaller-scale 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 dilution (in alkaline solutions, H2O, and in contact with
geological media) contains spherically-ripened monodisperse clusters. Uranyl peroxide nanoclusters were present in solutions at
near-neutral 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 ∼16.2 Å, in
excellent agreement with that obtained from the solid-state structural
data. Verification of the existence and stability of the 24-polyhedral
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).
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Groundwater flow investigations in geological systems aim to model
certainty over large timescales (1 m 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 is 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 an 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 inferred 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.
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Phase composition of the murataite-based ceramics containing 10 wt.
% ThO2, UO2, Nd2O3 and PuO2 and leaching of actinides using an
MC-1 procedure were studied. The ceramics were prepared by
melting of oxide mixtures in Pt ampoules at ~1500 OC. They are
composed of predominant phases of the pyrochlore-murataite series
and traces of extra phases (rutilite, chricotite, perovskite). Normally
three murataite-related phases with five-, eight-, and three-fold
primary 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 chricotite whereas the ceramic
produced at lower temperature (1400 OC) contained rutilite. The
Nd- and Pu-doped ceramics are also composed of major of the 5C and 8C
phases and minor rutilite. 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
MC-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/(cm2day).