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Solid State Physics of Transuranics

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DISCLAIMER

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Solid State Physics of Transuranics

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Abstract:
The experimental validation of first principals calculations of plutonium and its alloys is an important part of LLNL's science-based stockpile stewardship mission. This project has addressed this issue in the following ways. We have measured the electronic structure of U, Pu, and their alloys using valence band photoemission (PES), Soft X-Ray Fluorescence (SXF), and X-Ray Absorption Spectroscopy (XAS). In the long term, this will allow a direct comparison between calculated and measured density of electronic states, identifying the degree of f-electron localization in the alloys, and thus, permit selection of the best modeling code.

Introduction:
In recent years, the focus of the Laboratory has turned towards a science based approach to evaluate and predict the life-span and long-term safety of the nuclear stockpile. To this end, a great many modeling and measuring efforts are underway to address these concerns. This project from the Glenn T. Seaborg Institute for Transactinium Science (ITS) in the Isotope Sciences Division (ISD) of C&MS addresses a fundamental component of this science based stewardship endeavor: The experimental validation[1] of first principals calculations[2,3,4] of uranium, plutonium and their alloys that are the basis of many stockpile systems models.

We will perform these tasks in the following ways. We will generate validation data for first principals calculations of U, Pu and their alloys by measuring the electronic structure (Density of States – DOS) of the material using PES, SXF, and XAS. This will allow a direct comparison between calculated and measured density of electronic states and thus permit selection of the best modeling code needed for further materials property determination. This project also develops the stringent materials handling procedures for the synchrotron radiation techniques at the core of the project – techniques that will prove to be valuable to broader stockpile related missions.

Approach:
Ab initio, or first principal calculations of actinides and their alloys are performed to predict their equations of state. The results of the first principals calculations produce a density of electronic states for the material which can then be used to predict the macroscopic properties and behavior of the material under many conditions. While many projects are underway to validate experimentally[5] the structure of the actinides (high pressure x-ray diffraction, for example), no direct validation of the first steps in the calculation cycle are performed at LLNL. The most direct way to validate the results of the initial calculations is to measure the electronic structure of the materials[6] as a function of phase or alloy composition. We can do this with valence band photoemission and SXF to determine the occupied electronic states and XAS for the unoccupied or empty states.

Current approaches to modeling the electronic structure of Pu, its alloys, and other transuranics rely on the local density approximation (LDA)[2,3]. This approach has been useful

in modeling many other metals and alloys, but suffers from the limitation that it does not include enough of the electron correlation needed to accurately describe heavy elements (i.e., the strong relativistic effects). Various attempts to overcome this limitation with an adjustable "correlation" parameter in the LDA have led to fairly accurate interatomic distances for α-Pu and δ-Pu, albeit with a somewhat unphysical adjustable parameter. It is still unclear if these approaches will be suitable for phase stabilized alloys of Pu, and their improvement is the focus of current ASCI projects. Our goal in this portion of this project has been to measure the electronic structure of U, Pu, and their alloys to compare to current state of the art calculations and pending calculations on alloys.

One interesting phenomenon that we will be looking for is the localization of the 5f electrons in the alloys of Pu which should have intermediate electronic properties between itinerant (delocalized) 5f electrons in Pu and the lower actinides, and localized 5f (Kondo effect) electrons in Americium.[7] Earlier photoemission work[8] on U, Pu, and Am observed the localization in Am, but saw itinerant behavior in the α-Pu. The degree of localization for the 5f electrons in Pu alloys has direct bearing on the macroscopic properties of these materials (such as heat capacity) and thus underlies the importance of this project to measure the electronic structure of these materials as a means of model validation. Our measurements will be able to provide serendipitous Coulomb-interaction information that will be useful for theorists to refine the correlation correction to their models.

The challenge for this experimental program has been the difficulty of preparing and measuring clean Pu and Pu alloy surfaces that are complicated by severe safety concerns. These surfaces, especially those of Pu, are extremely reactive creating a surface layer that can obfuscate the desired bulk electronic structure measurement. Understanding the relationship of the electronic structure modification with alloy formation on this surface reactivity drives our experiments on U and its alloys. Other groups that characterize Pu and other actinides using a tunable photon (5-250 eV) plasma source photoemission apparatus produced noisy data that obscure the localization information sought.

Instead, we have overcome the significant technical obstacle of surface preparation by relying heavily on the SXF and XAS techniques. These methods probe the occupied and unoccupied electronic DOS of a material with elemental specificity – something that PES cannot do. These photon-in, photon-out techniques allow us to prepare encapsulated or coated samples in an inert/vacuum environment to protect and passivate the highly reactive U or Pu, and transport the materials to the synchrotron radiation facility. This procedure also greatly reduces the safety concerns surrounding this experiment – thereby reducing costs as well. The synchrotron radiation experiments will be performed at the Advanced Light Source – LBNL, and the Stanford Synchrotron Radiation Laboratory.

Milestones Accomplished:

We have begun the synchrotron radiation SXF and XAS experiments in the first half of FY'98 and have made significant progress in developing the radioactive materials preparation, handling, and analysis procedures needed for the success of this project. We have measured the SXF of U, UO_2, and UO_3 samples at the ALS, and U and U-Nb alloys at SSRL. Initial

interpretation of these results indicate that our samples preparation methods are producing unreacted surfaces that remain pristine throughout the experiment. These results also indicate that we can see evidence for charge transfer in the alloy.

We have successfully performed XAS experiments on the alpha and delta phase of plutonium in FY99. Initial interpretation of these results, indicate that our samples preparation methods are producing unreacted surfaces that remain pristine throughout the experiment. These results also indicate that we can see evidence for charge transfer in the alloy that will be critical for accurate interpretation of the coulomb effects in Pu and its alloys. Pictured in figure 1 is a comparison of the core level photoabsoption near edge structure from alpha (lower curve) and delta (upper curve) plutonium. The difference in near edge structure is a direct sampling of the difference in empty electronic states in the two phases of plutonium and can be interpreted as evidence of charge transfer in select phases of plutonium. These results are consistent with our earlier work on U and Nb-U alloys where a similar charge transfer was observed.

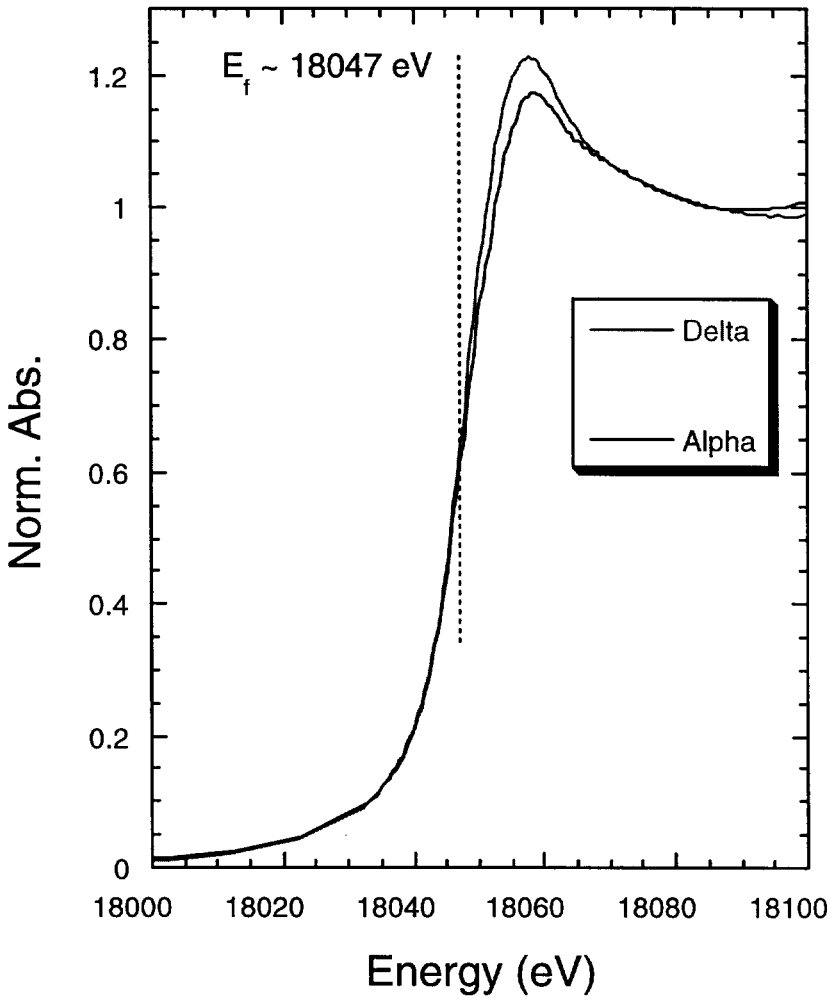

Figure 1: the core level photoabsoption near edge structure from alpha (lower curve) and delta (upper curve) plutonium measured at the Stanford Synchrotron Radiation Laboratory.

Benefit:

The primary, and long term, benefit of this project to Lawrence Livermore National Laboratory is in validating the initial steps of the modeling cycle for weapons systems - a modeling cycle that will be asked to predict performance and safety of extended life-span materials, and in determining the actual mechanical property and structural changes that may occur in extended life materials. The immediate benefit of this project has been in the creation of an Enhanced Surveillance Program project on this topic that is directly funded by DNT.

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