# ESC FY2002 Annual Report: Synchrotron-Radiation-Based Photoelectron Spectroscopy at the Advanced Light Source

*J. G. Tobin, B. W. Chung, R. K. Schulze, D. K. Shuh*

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# ESC FY2002 Annual Report: Synchrotron-Radiation- Based Photoelectron Spectroscopy at the Advanced Lights Source

**PI: J.G. Tobin**
**Collaborators: B.W. Chung, LLNL;  R.K. Schulze, LANL; D.K. Shuh, LBNL**

## Overview

Despite recent intensive experimental effort [1-3], the electronic structure of Pu, particularly $\delta$-Pu, remains ill defined.  An evaluation of our previous synchrotron-radiation-based investigation of $\alpha$-Pu and $\delta$-Pu [1] has lead to a new paradigm for the interpretation of photoemission spectra of U, Np, $\alpha$-Pu, $\delta$-Pu and Am.  This approach is founded upon a model in which spin and spin-orbit splittings are included in the picture of the 5f states [4] and upon the observation of chiral/spin-dependent effects in non-magnetic systems. [5,6]    By extending a quantitative model developed for the interpretation of core level spectroscopy in magnetic systems [7], it is possible to predict the contributions of the individual component states within the 5-f manifold.  This has lead to a remarkable agreement between the results of the model and the previously collected spectra of   U, Np, Pu and Am, particularly $\delta$-Pu,  [1-3,8]  and to a prediction of what we might expect to see in future spin-resolving experiments. [9]    This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

1. J. Terry, et al,  Surface Science Letters 499, L141 (2002).
2. T. Gouder, et al, Europhys. Lett. 55, 705 (2001); MRS Bulletin 26, 684 (2001); Phys. Rev. Lett. 84, 3378 (2000).
3. A.J. Arko, et al, , Phys. Rev. B 62, 1773 (2000).
4. S.Y. Savrosov and G. Kotliar, Phys. Rev. Lett. 84, 3670 (2000).
5. Ch. Roth et al, Phys. Rev. Lett. 73, 1963 (1994).
6. K. Starke et al, Phys. Rev. B 53, 10544 (1996).
7. J.G. Tobin and F.O. Schumann, Surface Science 478, 211 (2001).
8. J.R. Naegele, "Photoem. of Solids," Landolt-Bornstein III/B,183 (1994).
9. J. Tobin, et al, "Photoelectron Spectroscopy of Plutonium at the Advanced Light Source",  UCRL-JC-145703, J. Nucl. Sci. Tech./ Proc. of Actinides 2001, accepted 2002.

## Indicators of Quality of Work:Publications

1.   J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelmann, E. Rotenberg, D.K. Shuh, G. van der Laan, D.A. Arena,  and J.G. Tobin, "5f Resonant Photoemission from Plutonium,"  Surface Science Letters 499, L141 (2002).

2.  J.G. Tobin, D.A. Arena, B. Chung, P. Roussel,  J. Terry, R. K. Schulze, J. D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, and D. K. Shuh, "Photoelectron Spectroscopy of Plutonium at the Advanced Light Source ",  UCRL-JC- 145703, J. Nucl. Sci. Tech./ Proc. of Actinides 2001, accepted, August  2002.

3.  J. Tobin, et al, "Resonant Photoemission in f Electron Systems:  Pu & Gd", UCRL-JC-146496, under preparation.

## Indicators of Quality of Work: Invited talks by JG Tobin on this subject.

1. March Meeting of the Amer. Phys. Soc., Indianapolis, IN, March 18-22, 2002
2. Pu Workshop, VNIIEF, Sarova, Russia,  June 25-27, 2002.
3. 6th Prague Colloquium on f Electron Structure, Prague, The Czech Republic, July 5-8, 2002.

**Motivation: Experimental benchmarking for Input to Models of Pu Aging**

Many of the input parameters for Aging Models are not directly measurable. These parameters will need to be calculated or estimated. Thus we need a First Principles-Approach Theory, but it is unclear what terms are important in the Hamiltonian. ($H\Psi = E\Psi$) Therefore, we need experimental data concerning the 5f electronic structure, to determine which terms in the Hamiltonian are important. Goal: Correct Fundamental Theory for Pu, including Pu Alloys & Pu Phases. Tool: Double Polarization Photoelectron Spectroscopy (DPPS), which includes chiral excitation and spin-resolving detection. Underlying question: does the spin polarized description capture the essential physics?

**Problem: There is no single, atomistic model for both alpha and delta Pu, nor direct experimental verification.**

Alpha-Pu is monoclinic, more dense and supposedly more free-electron-like. Delta-Pu is face-centered cubic, less dense and supposedly a correlated-electron material. There is a 20% volume change between $\alpha$ and $\delta$. There are no maps of either binding energy of the bands (Ag(111)-PRB 32, 3465(1985))) or Fermi crossings (YBCO-PRB 45,5563 (1992)) versus momentum for either phase. (No single crystals…) It is incorrect to assume that a single photoemission spectrum represents the DOS. Photoemission spectra change with energy and angle and there are matrix element effects… <u>Need a new approach!</u>

**New Paradigm: It is possible to have spin sensitivity in non-magnetic samples, using Double Polarization Photoelectron Spectroscopy.**

Cu 3p with Linear Polarization:
Kisker et al, Phys. Rev. Lett.
73, 1963 (1994).

W 4f with Circular Polarization:
K. Starke et al, Phys. Rev. B
53, 10544 (1996).

**New Paradigm: Digression to Core Level Spectroscopy in Magnetic Systems**

There are dichroic and spin-dependent effects due to the internal structure of these photoemission peaks and core levels. To the right: X-ray Magnetic Linear Dichroism of FeCo/Cu(001). [ See Phys. Rev. Lett. 79, 5166 (1997) and Surf. Sci. 478, 211 (2001).] The comparison of the FeCo/Cu(001) dichroism experiment and theory is also shown here. The match using this simple theory is very good.
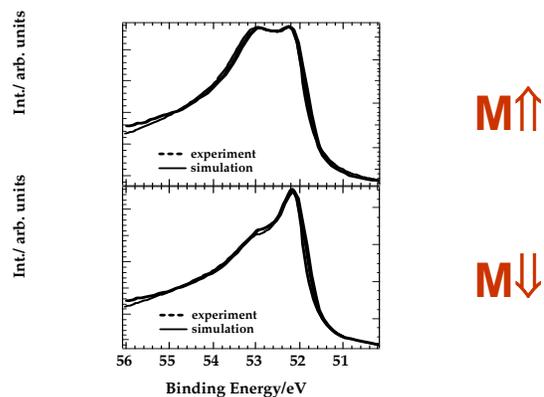
**New Paradigm:The Internal Structure is due to S-O and Exchange splittings.**

The internal structure of these core - levels is due to the interaction of spin-orbit and exchange splitting, complicated by the multi-electronic Doniach-Sunjic lineshape.

Right: (top) The energy positions of the Fe 3p components, split by exchange and spin orbit; (middle) DS lineshapes; (bottom ) the DS asymmetry. Below: The energies of the orthogonalized 3p states, versus exchange (Hs) and spin orbit ($\zeta$).
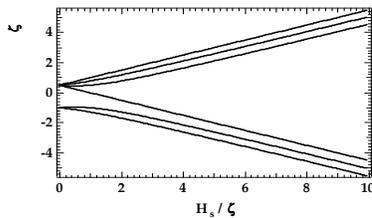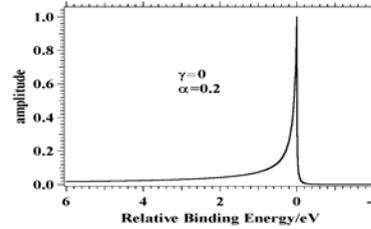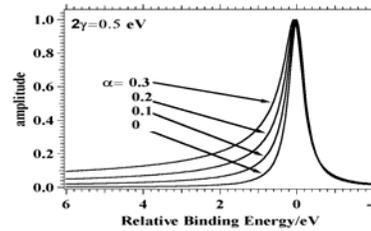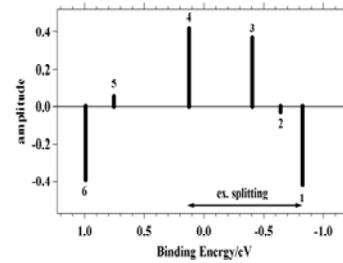
**New Paradigm: try to analyze the 5f valence states with this picture.**

The recent results of Savrasov and Kotliar et al point in this direction: Phys. Rev. Lett. 84, 3670 (2000). [Also see Soderlind, EuroPhysics Letters 55, 525 (2001).] The salient result is metallization with the retention of "flat-bands, i.e., atomic-like 5f states.  These 5f states are spin and orbital momentum specific, just like the components in the Fe3p manifold.  Here, the spin and orbital moments tend to cancel each other, giving a nominally non-magnetic $\delta$ Pu. Cancellation of spin and orbital magnetism in actinides has been observed experimentally, e.g. Lander et al PRB 39, 4719 (1989).

## Comparison of experiment and theory for δ-Pu (n = 5.1)

Our experimental result is shown at the right-top.  Here, the spectra were taken at a photon energy of 125eV. Spectra for two samples are shown: δ-Pu and δ/α- Pu , which is bulk α-Pu with a δ-Pu reconstruction on the surface.  (This is following Gouder et al, EuroPhysics Letters.) Soderlind, Landa and Sadigh predict that the δ-Pu is antiferromagnetic at low temperature with a magnetic moment of 1.5 μB due to partial cancellation of large spin and orbital moments.  At higher temperatures, they predict that δ-Pu is a disordered paramagnet.  Reymond and Fournier [J. Alloys. Cmpds. 232, 199(1996)] have reported paramagnetic μ-eff in Ce and Ga stabilized δ-Pu of 1.7 μB and 1.2 μB, respectively. Using the above as a guide, we have applied our simple model to this problem.  As can be seen from the middle panel, there is significant agreement between the intensity predicted by this simple model and our experimental results. To observe dichroic effects, the disordered paramagnetic δ-Pu would require a double-polarization experiment, with both a chiral probe and true spin detection. The relative magnitude of the dichroism will depend upon the specifics of the experiment.

**In the bottom panel, we plot the prediction of a Double Polarization Effect in disordered, paramagnetic δ-Pu**
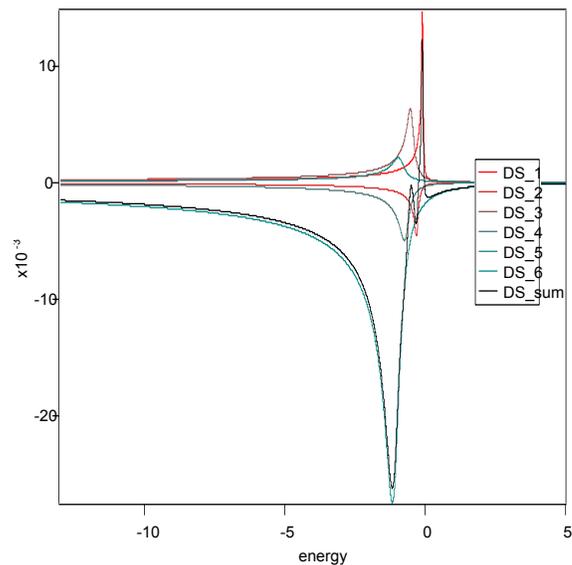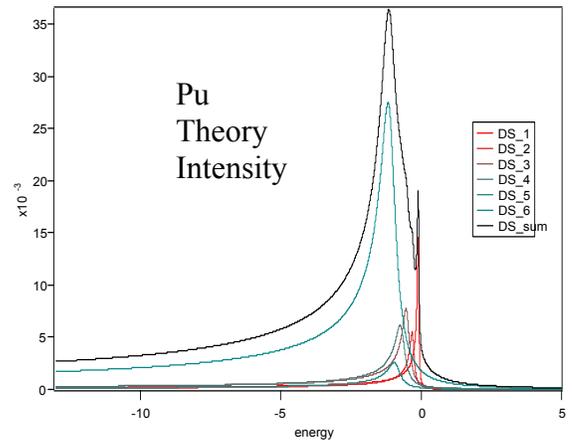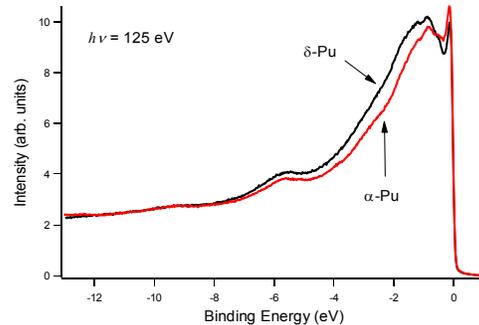
Intensity

**Quantitative agreement of moment cancellation with previous results.**

From our model, we can calculate the spin, orbital and total moments versus Hs/$\zeta$,, assuming the Pu 5f electrons are metallic and do not experience angular momentum coupling,i.e., following Savrosov and Kotliar. Soderlind, Landa and Sadigh: $\mu$ = 1.5$\mu$B. Reymond and Fournier, [J. Alloys. Cmpds. 232, 199(1996)] : $\mu$ = 1.2 $\mu$B -1.7 $\mu$B. Savrosov and Kotliar, [Phys. Rev. Lett. 84, 3670 (2000)]: $\mu$ = 1.2 $\mu$B In the range of Hs/$\zeta$ near zero, we are in agreement with the above predictions. Our best estimate is x = 1.6 which gives $\mu$ = 1.3 $\mu$B.

$$L = \sum <li>$$

$$\mu = L + 2\,S$$

$$S = \sum <si>$$

$$X = Hs/\zeta$$
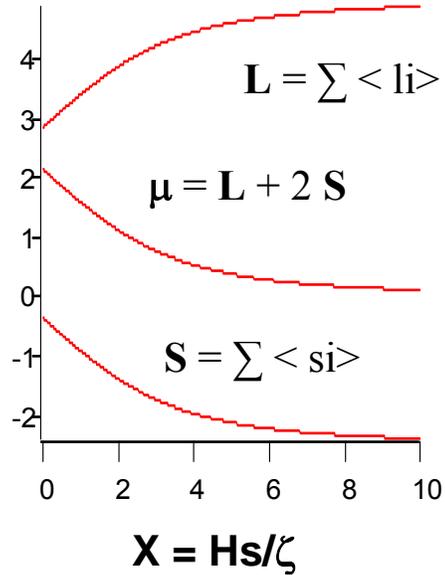
**We are building a dedicated, spin-resolving spectrometer for the study of Pu, with sophisticated safety features.**

Hepa Filter

Spectrometer

Vacuum Suitcase

Mini-Mott for spin resolution

Alpha detectors, not shown, will also be placed throughout the spectrometer.

LLNL ESC Annual Report-FY02

ESC Task:              LL-61

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                       (Photoelectron Emission Spectroscopy)

MTE Supported:      MTE/Project: Pits/Lifetime Task LL-01

Type of Task:        Diagnostic

PI:            Bill Wolfer/ Jim Tobin
Contributors: B.CHUNG1, R. K.SCHULZE2, and D. K. SHUH3,
1.Lawrence Livermore National Laboratory, Livermore CA
2.Los Alamos National Laboratory, Los Alamos NM
3.Lawrence Berkeley National Laboratory, Berkeley, CA

Deliverable to ESC:
The nature of the electronic structure of alpha and delta Pu

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Pu Spectrometer
LLNL: Vacuum and Sample Transfer, Spin-Resolution
LBNL: Safety and Pu Sample Handling, Photoelectron Analyzer ($120K), Ar+ Source ($50K), in house support labs
LANL: Pu Samples and laboratory x-ray source ($60K), Pre-cleaning facility in Bldg 70A
Karlsruhe: Vapor deposition of U and Pu