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Observation of Dynamical spin shielding in Ce: Why It Matters for Pu Electronic Structure

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37th Journees des Actnides
Sesimbra, Portugal
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Collaborators

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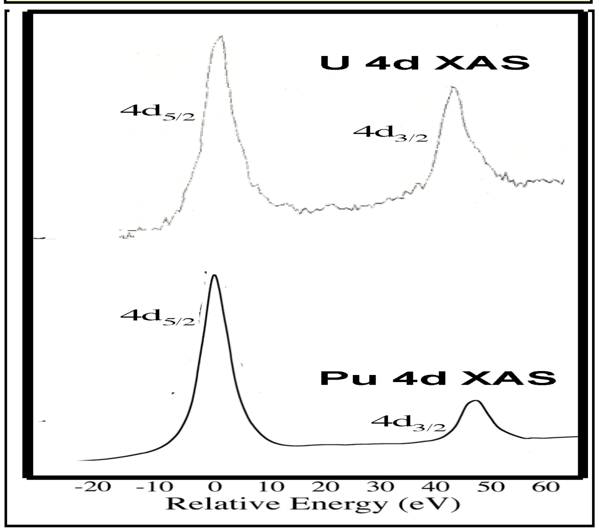
Unraveling the Enigma of Pu Electronic Structure

In a series of experiments and linked theoretical modeling, the range of possible solutions for Pu electronic structure has been dramatically reduced.

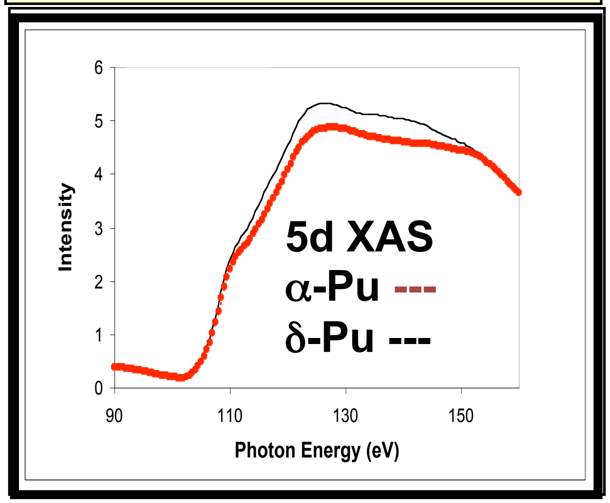
Nevertheless, the key issue of electron correlation remains.

5f Spin Orbit Coupling is large
Pu has a large neg <w110>



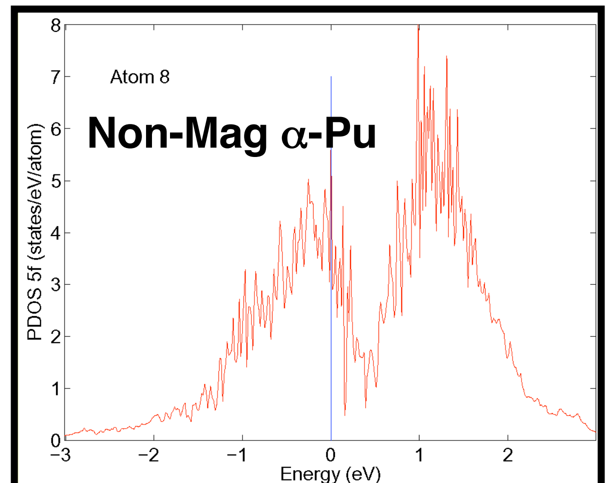
G. van der Laan, K.T. Moore, J.G. Tobin, B.W. Chung, M.A. Wall, and A.J. Schwartz, ,"Applicability of the spin-orbit sum rule for the actinide 5f states," Phys. Rev. Lett. 93, 097401 (Aug 2004).

The number of 5f electrons is 5 (no pre-peak in Pu)



K.T. Moore, M.A. Wall, A.J. Schwartz, B.W. Chung, D.K. Shuh, R.K. Schulze, and J.G. Tobin, "The Failure of Russell-Saunders Coupling in the 5f States of Plutonium", Phys. Rev. Lett. 90, 196404 (May 2003).

V_{SO} > $V_{Delocalization}$
Two lobes in the 5f pDOS

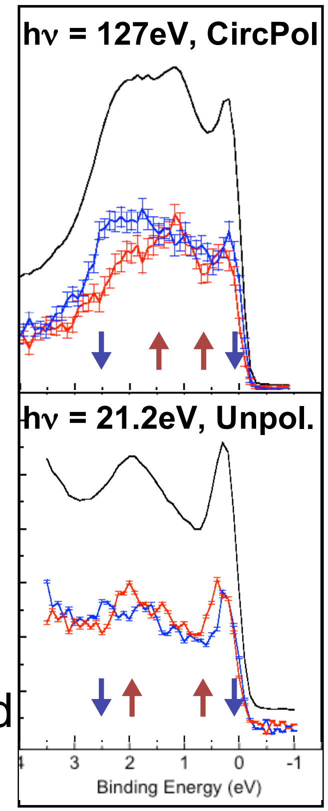


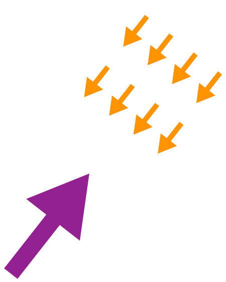
J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, "Competition Between Delocalization and Spin-Orbit Splitting in the Actinide 5f States," Phys. Rev. B, 72, 085109 (Aug 2005).

Preview: Proof of Spin Shielding in Ce

- **Using spin-resolved PES of non-magnetic Ce, reversed phases are observed between the Lower Hubbard Band (BE = 2 eV, ↓↑) and the Quasiparticle Peak (BE = 0 eV, ↑↓)**
- **Now, let’s walk through the process of how we arrived at this result.**

Fano Effect in polycrystalline Ce

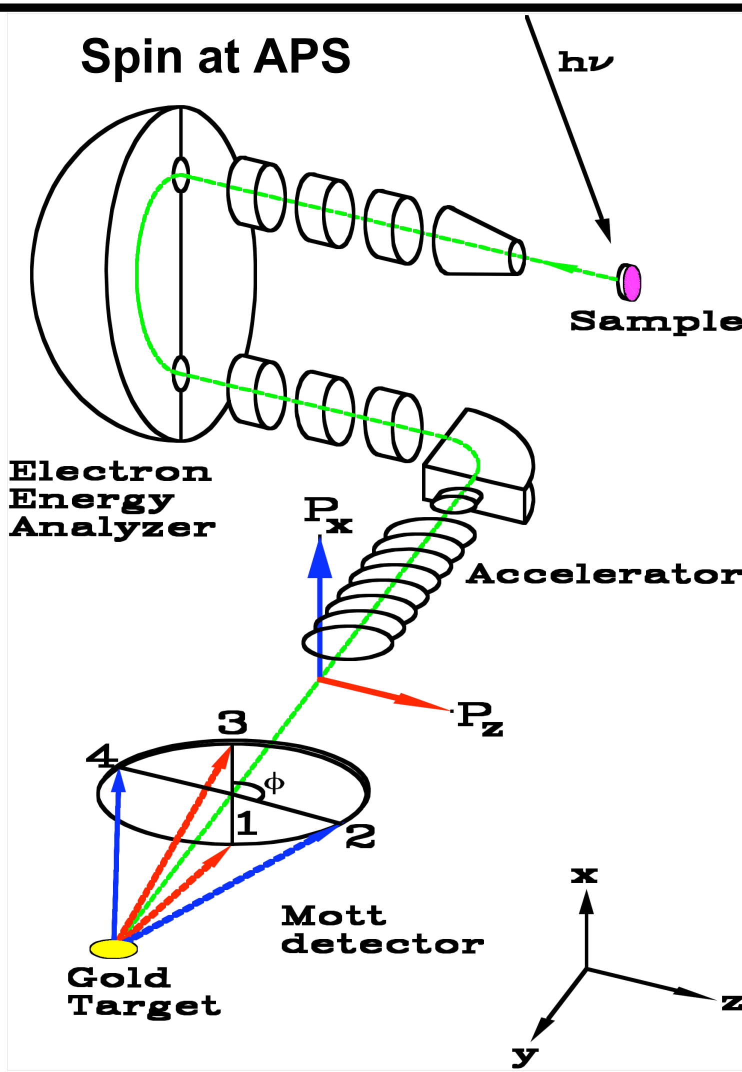




Jim’s Imperfect Interpretation of Kondo Shielding and the Gunnarsson-Shoenhammer Model

The spins of the QP electrons ↑ collectively shield the spin of the LHB ↑ electron. This is a dynamic process, with zero net mag moment on the Ce.

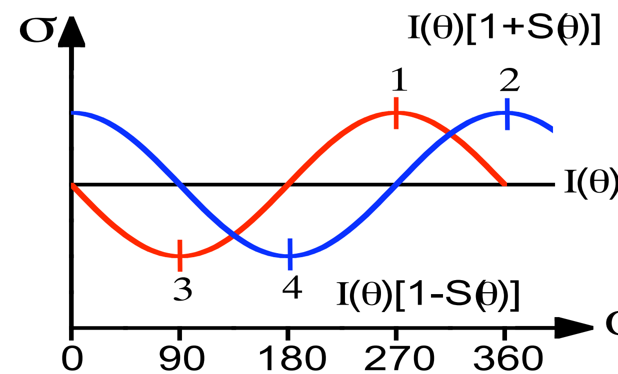
Instrumentation & Experimental Possibilities



Three Spin Resolving Spectrometers:
(1) "Spin" at BL 4 at the APS
(2) "UMR" at BL 4 at the ALS
(3) "Actinide" at LLNL

$$\sigma(\grave{e},\phi) = \mathrm{I}(\grave{e})[1 + S(\grave{e})\tilde{\mathrm{N}}\cdot\hat{\mathbf{n}}]$$

$$\hat{\mathbf{n}} = \frac{\mathbf{k}\times\mathbf{k}'}{|\mathbf{k}\times\mathbf{k}'|}$$



Electron Correlation in Ce

- **Much of the controversy revolves around the interpretation of the Ce photoemission structure in terms of a modified Anderson Impurity Model, first put forth by Gunnarsson and Schoenhammer (PRL and PRB 1983). Here, in this correlated and multi-electronic picture, semi-isolated 4f states (at a nominal binding energy of 1 eV) are in contact with the bath of spd valence electrons, generating spectral features at the Fermi Level and at a binding energy corresponding to the depth of the bath electron well, about 2 eV below the Fermi Level in the case of Ce.**
- **To the right, a re-visitation of the issue, from Kotliar and Vollhardt, Physics Today, March 2004.**

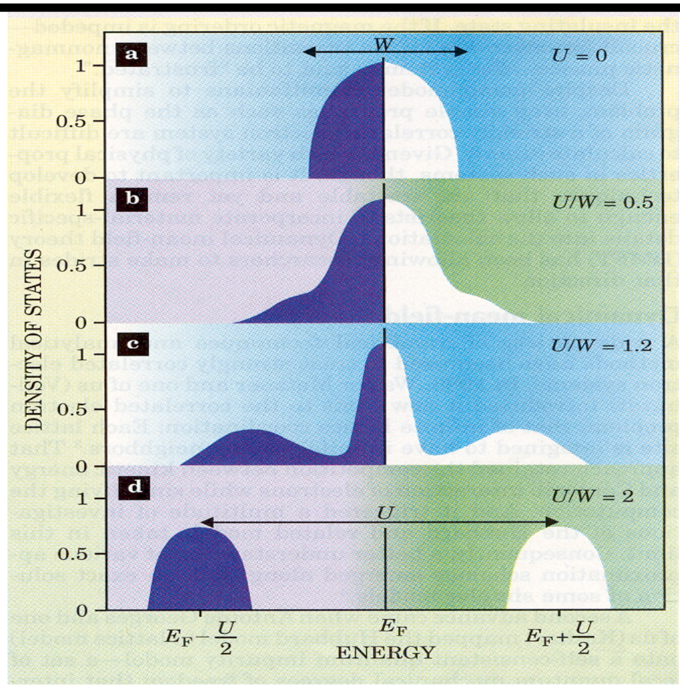
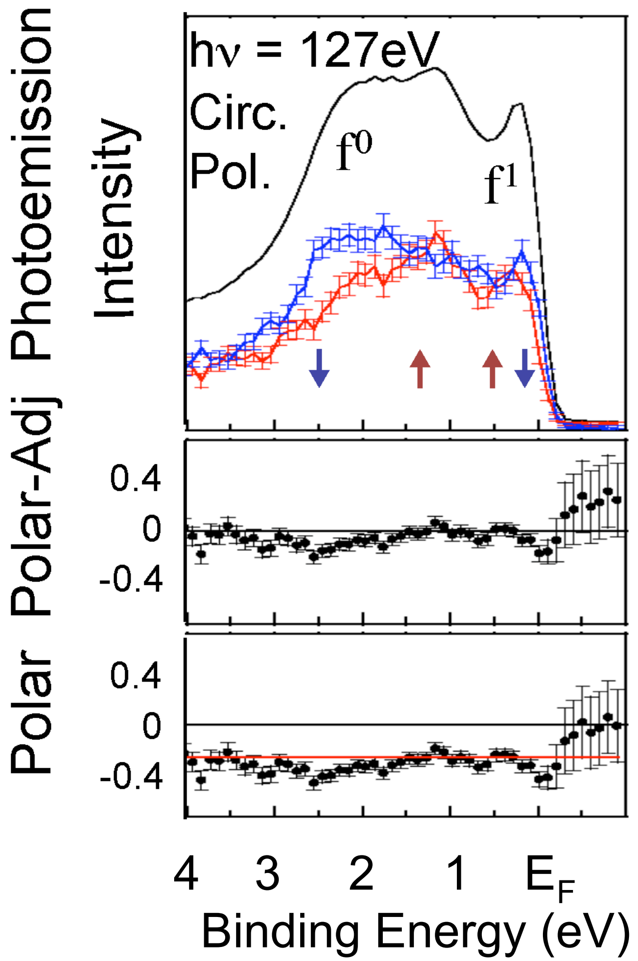


Illustration of the origin of the quasiparticle (at the Fermi Level, E_F) and t he Hubbard Bands (at $\pm$ U/2, relative to the Fermi Level). W is the band width and U is the correlation strength. Case c, third from the top, is the case closest to Ce.

Spin-Res Resonant Photoemission from the ALS: The polarization shows an intriguing oscillation, if the static polarization is simply subtracted off. (Justification:Yu et al PRB06)

Static Polarization Removed



There are strong spin dependent effects in the valence states of Ce

- **The peak at BE = 2 eV (f^0 final state, Lower Hubbard Band) has a phase where up leads down.**
- **The peak at the Fermi Level (BE near 0, f^1 final state, Kondo peak) has the reverse phase, where down leads up.**

However, we need to confirm this result with an off-resonant measurement!

The Fano Effect:

U. Fano, Phys. Rev. 178, 131 (1969); 184, 250 (1969);

U. Heinzmann, J. Kessler, and J. Lorenz, Phys. Rev. Lett. 25, 1325 (1970).

The equivalence of the information from XMCD and XMLD in PES is well established.

- **In XMLD, a chiral configuration of linear vectors substitutes for the intrinsic handedness of the circularly polarized light.**
- **The relationship between the Linear and Circular dichroic variants of PES have been discussed by many, including Venus and van der Laan**

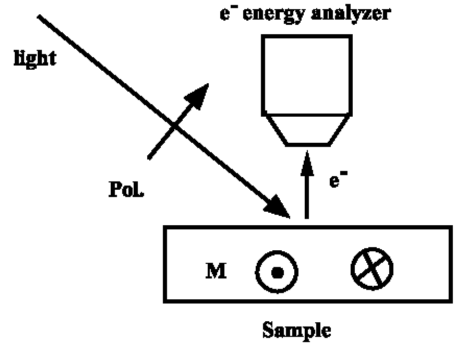


Fig. 1. Diagram of dichroism experiment, with photoelectron emission along the surface normal (z). Here the magnetization is in the surface plane but perpendicular to the yz plane containing the electron emission direction and the Poynting vector and linear polarization vector (E) of the X-rays. α is the grazing angle of incidence between the incoming photon and the surface plane. The magnetization (M) defines the sign of the $+x$ axis. The $+y$ axis is determined by the right hand rule from $+z$ and $+x$. Magnetization reversal does not affect z but rather flips $+x$ and thus $+y$.

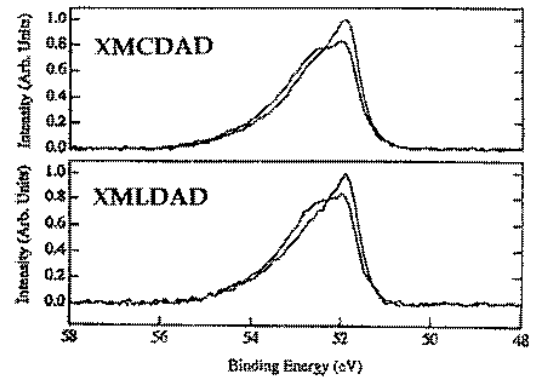


Fig. 4. Comparison of the circular (XMCDAD) and linear (XMLDAD) photoemission dichroism for 6 ML of $Fe_{50\%}$-$Ni_{50\%}$/Cu(0 0 1), with x along [1 0 0], 45° from the easy axis along [1 1 0]. The photon energy was 95 eV. Backgrounds have been subtracted from the experimental curves. Note that both peak asymmetries are 11.4%, where asymmetry is $A = (I^+ \quad I^-)/(I^+ + I^-)$. See Refs. [26,27] for details.

Tobin and Schumann,
Surface Science 478, 211 (2001)

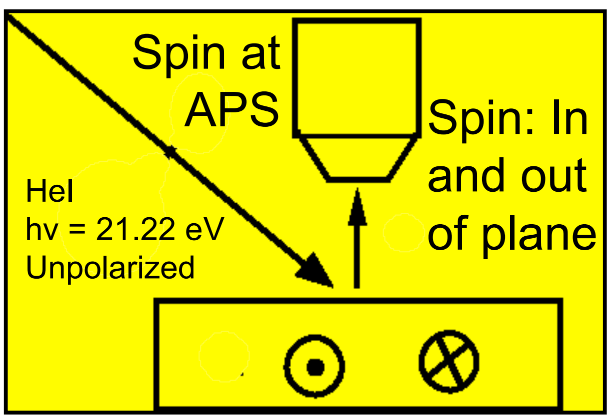
In the the case above, the XMCD and XMLD correspond to the imaginary and real parts of the same matrix element.

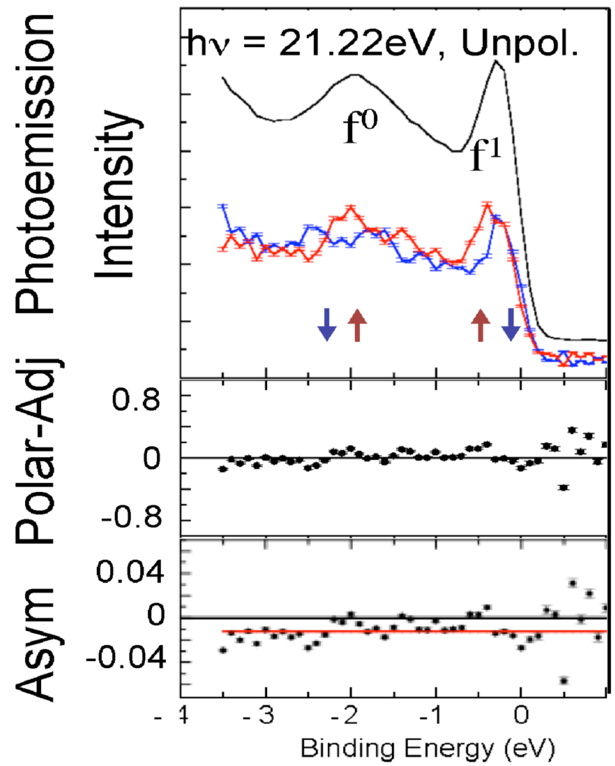
Direct Photoemission of Ce: Fano Effect measurement with He I and spin detection

$$\text{Polarization}_{\text{Unpol}} = P_U \propto [(I^{\uparrow}_{+})^{1/2} - (I^{\downarrow}_{+})^{1/2}] \;/\; [(I^{\uparrow}_{+})^{1/2} + (I^{\downarrow}_{+})^{1/2}]$$

Again, there strong spin dependent effects in the valence states of Ce

- **Again, the peak at BE = 2 eV (f^0 final state, Lower Hubbard Band) has a phase where up leads down.**
- **Again, the peak at the Fermi Level (BE near 0, f^1 final state, Kondo peak) has the reverse phase, where down leads up.**





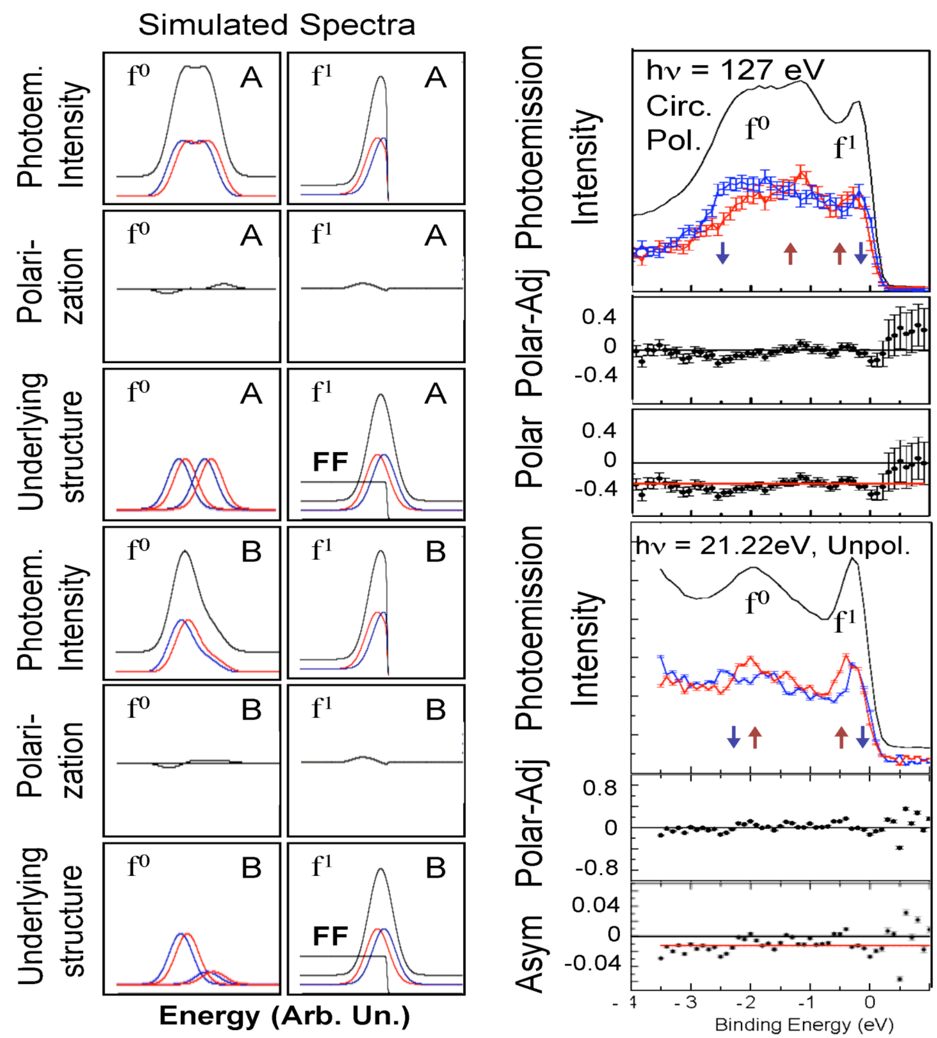
These spectra directly confirm the ResPes results at hv = 127 eV.

The static asymmetry offset was subtracted as a correction for instrumental asymmetry.

Note: Because the chirality is induced via the geometrical configuration of vectors, it is impossible for us to flip the "helicity" for now…

Interpretation: We can model the results with our simple theory, following the Au example.

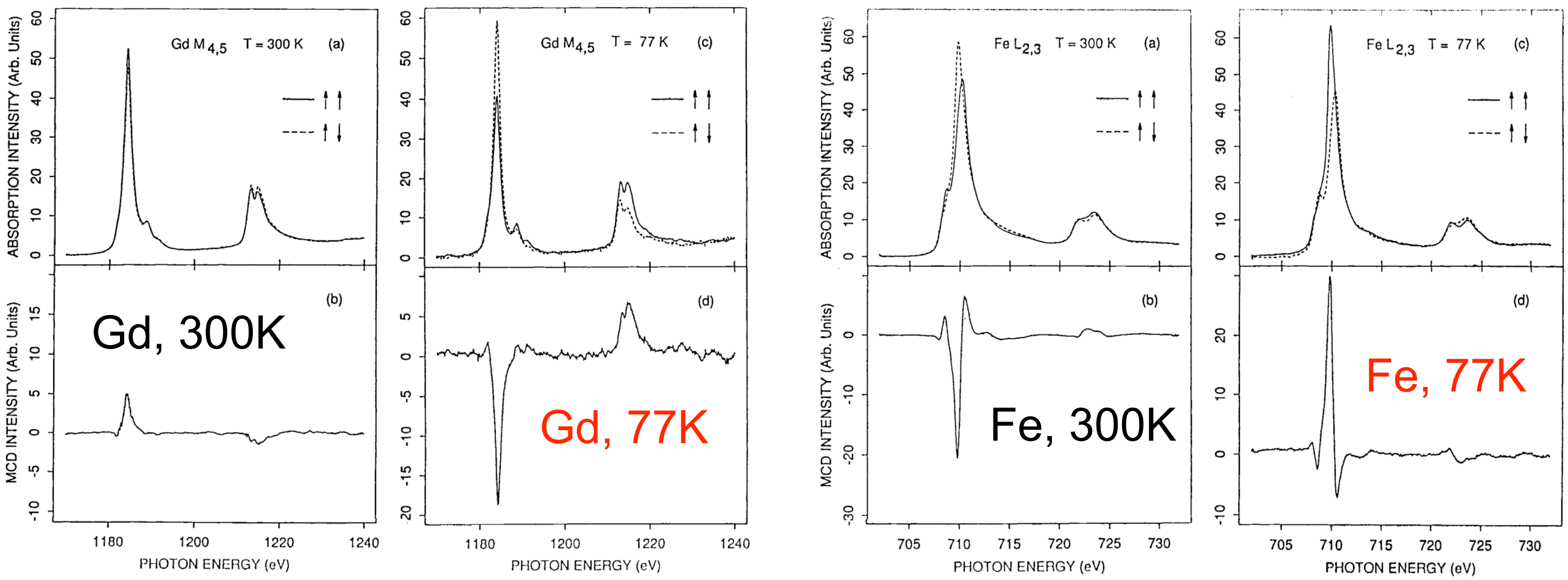
- **The peak at BE = 2 eV is actually composed of two sub-peaks, with the relative intensities varying with photon energy. The two peak postulate is consistent with earlier observations by Jensen and Weiliczka, PRB 1984 and Vyalikh et al, PRL 2006.**
- **The peak at the Fermi Level (BE near 0, f^1 final state, Kondo peak) must be truncated properly with the Fermi Function. This means that the peaks look less like shifted peaks and more like overlapping peaks with different widths.**
- **The underlying structure is that the peak at the Fermi Energy has a reversed phase relative to the peak at 2 eV…but what does this mean?**



What do we know about phase reversal?

Phase Reversal and AntiFerromagnetic Coupling: The case of Fe and Gd in the Garnet, Gd3Fe5O12

The Fe ensemble and Gd are antiferromagnetically coupled. At 300K, the Gd is disordered. At 77K the Gd is ordered, and the phase of the Fe signal reverses

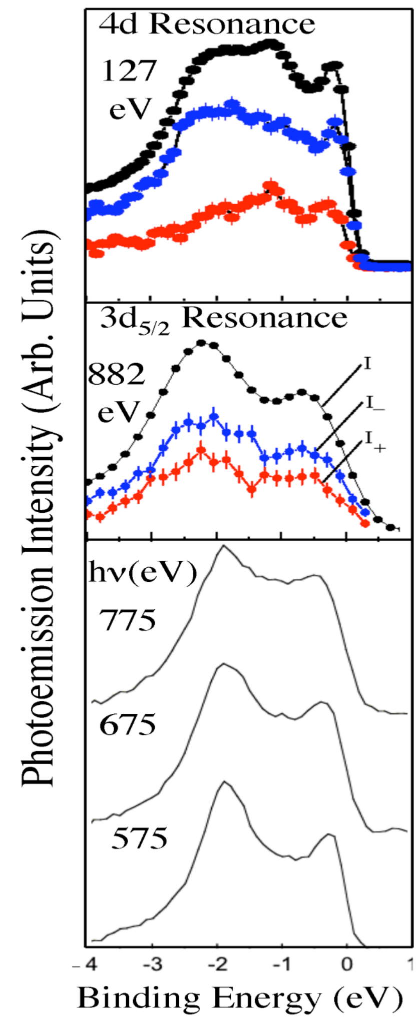


This is XAS-MXCD. Please see Tjeng et al, SPIE 1548, 160 (1991) for the details.

What do we know about the electrons in the peaks at BE = 2 eV and at the Fermi Level?

- **Both peaks have strong and roughly equivalent f character**
  - –This comes from the Resonant Photoemission at both hv = 127 eV and at hv = 882 eV. The Ce Resonant Photoemission exhibits an enhancement of the intensity due to the second channel that goes through the 4d or 3d core level state and is governed by dipole selection rules. Thus the enhancement is f selective and is a measure of f-character. Both states exhibit much the same enhancement and thus have substantial and roughly equivalent f-character.

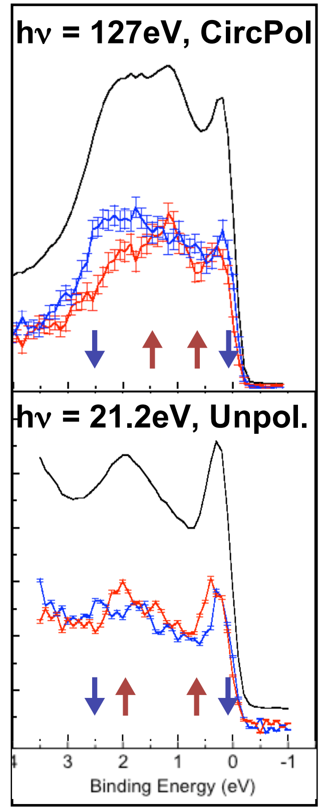
- **Both peaks have strong and roughly equivalent bulk character**
  - –Following the lead of Mo et al (PRL 2002), we have made measurements over a wide range at fairly high photon energies. Again, both states exhibit much the same intensities, indicating strong and equivalent bulk character.



Summary: Proof of Spin Shielding in Ce

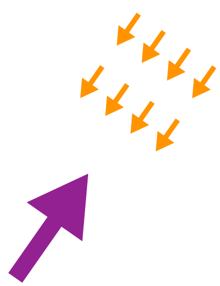
- **Reversed phases are observed between the Lower Hubbard Band (BE = 2 eV, ↓↑) and the Quasiparticle Peak (BE = 0 eV, ↑↓)**
- **Both states have strong and roughly equivalent f-character and bulk character.**
- **Phase reversal is an indication of antiferromagnetic coupling.**
  - **Other complications can also flip the phase, but none of these can apply here. These electrons are located on the same atom, have the same character and experience the potential symmetry. Thus the only possible explanation of the phase reversal is a dynamic anti-alignment of the spins.**
- **Thus, what we have have is a proof of spin shielding in Ce and a confirmation of the models of electron correlation!**

Fano Effect in polycrystalline Ce



Reconciliation with the Model of Gunnarsson and Shoenhammer

- **Theory: The state at 2eV is an f electron and the state at E_F is of spd character.**
  - **In this correlated and multi-electronic picture, semi-isolated 4f states (at a nominal binding energy of 1 eV) are in contact with the bath of spd valence electrons, generating spectral features at the Fermi Level and at a binding energy corresponding to the depth of the bath electron well, about 2 eV below the Fermi Level in the case of Ce.**
- **Experiment: Both states have strong and roughly equivalent f character**
- **Reconciliation: Recent DMFT calculations by A. Georges et al (arXuv:cod-mat) suggest that electrons of the same character can shield themselves and that the iterative nature of DMFT will induce a mixing of the pure states characteristic of the earlier models of electron correlation.**



Jim's Imperfect Interpretation of Kondo Shielding and the Gunnarsson-Shoenhammer Model

The spins of the QP electrons ↑ collectively shield the spin of the LHB ↑ electron. This is a dynamic process, with zero net mag moment on the Ce.

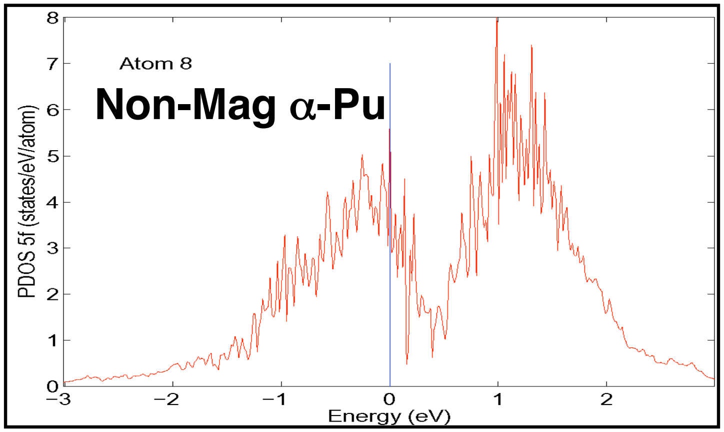
Resolving the electron correlation controversy in f-electron systems

Understanding f-electron correlation is the next step in resolving the electronic structure of Pu

Thus far, we have narrowed the parameter space for Pu with the following three experimental observations

1. 5f Spin Orbit Coupling is large
2. The number of 5f electrons is 5
3. $V_{SO} > V_{Delocalization}$

i. Phys. Rev. Lett. 90, 196404 (2003).
ii. Phys. Rev. Lett. 93, 097401 (2004).
iii. Phys. Rev. B 72, 085109 (2005).



The First Experimental Proof of Spin Shielding

These Fano Effect measurements (including both chiral excitation and true spin detection) and the observed result of reversed phases between the Kondo Peak and the Lower Hubbard Band demonstrate that there truly is spin shielding in nonmagnetic Ce, as predicted by Gunnarson- Shoenhammer, albeit in a Hubbard Model because both states have f-character.

Even more importantly, it shows us the way to proceed with Pu

Please see "Evidence of dynamical spin shielding in Ce from spin-resolved photoelectron spectroscopy,"

J.G. Tobin et al , EuroPhysics Letters (EPL) 77, 17004 (Jan 2007).

Fano Effect in polycrystalline Ce