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An Internal Report: Experimental Proof of Dynamical Spin Shielding in Ce from Spin-Resolved Photoelectron Spectroscopy

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Abstract

Using Fano Effect measurements upon polycrystalline Ce, we have observed a phase reversal between the spectral structure at the Fermi Edge and the other 4f derived feature near a binding energy of 2 eV. The Fano Effect is the observation of spin polarized photoelectron emission from NONMAGNETIC materials, under chirally selective excitation, such as circularly polarized photons. Within various models, the peak at the Fermi Energy (f^1 peak, quasiparticle peak, Kondo peak) is predicted to be the manifestation of the electrons which shield the otherwise unpaired spin associated with the peak at 2 eV (f^0 peak or Lower Hubbard Band). Utilizing high-energy photoelectron spectroscopy, on and off resonance, the bulk nature and f-character of both features have been confirmed. Thus, observation of phase reversal between the f^0 and f^1 peak is a direct experimental proof of spin shielding in Ce, confirming the original model of Gunnarsson and Shoenhammer, albeit within a Hubbard picture.

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Electron correlation is perhaps the last, great unknown in the study of the electronic structure of materials. The conventional experimental approach to the problem is to test the various predictions of different models by interrogating complex systems with photoelectron spectroscopy of very high energy and angular momentum. [1-3] Here, we report of a study performed in a different mode, wherein the central issue of most electron correlation models can be directly addressed, i.e. shielding of unpaired spins.   By performing photoelectron spectroscopy with a different type of high resolution, using chiral excitation and true spin resolution [4,5], it has been possible to probe directly the phase relationships of the valence band features in Ce. Below, it will be shown that the shielding of the unpaired spin (in the Lower Hubbard Band, LHB, or f^0 peak) by the electrons in the quasiparticle peak (f^1 or Kondo peak, near the Fermi Energy) has been observed in the case of polycrystalline Ce. (See Figure 1.)

Figure 1
Spin-resolved and spin-integrated spectra of polycrystalline Ce is shown here, along with corresponding polarizations and asymmetry data. Error bars for the spin-resolved spectra are included. Blue corresponds to spin down and red for spin up. See text for details.
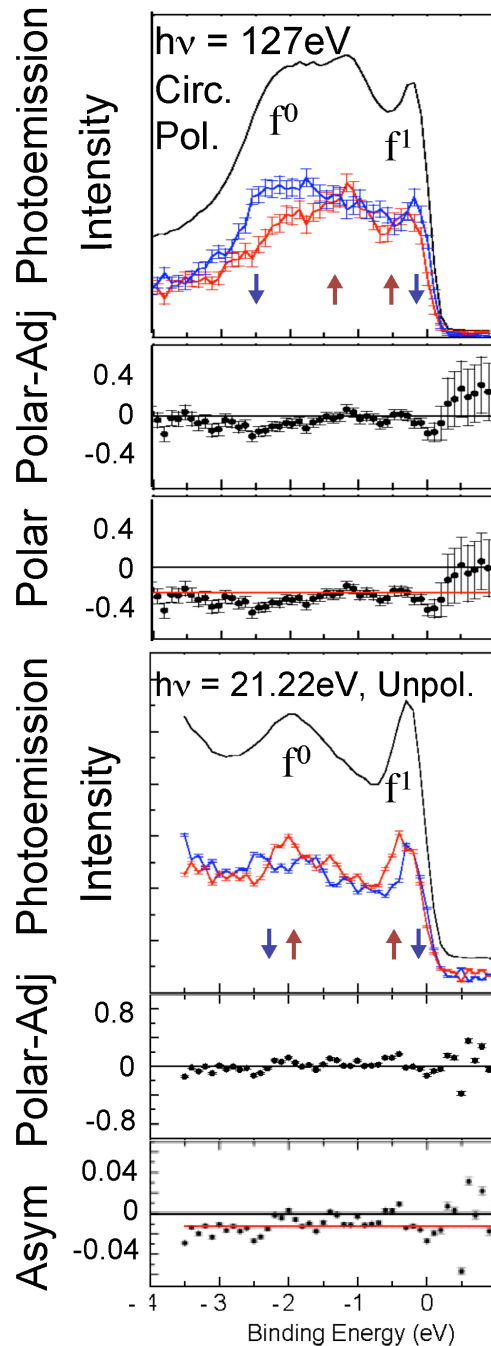
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For many years, the valence electronic structure (and corresponding electron spectra) of Cerium has remained a subject of uncertainty and controversy. Perhaps the best and most direct method of ascertaining the valence electronic structure is the application of electron spectroscopies [6-22], e.g. photoelectron spectroscopy for the occupied states [6 - 15, 17-19] and x-ray absorption [7] and Bremstrahlung Isochromat Spectroscopy (inverse photoelectron spectroscopy) [8,16,18] for the unoccupied states. Much of the controversy revolves around the interpretation of the Ce photoemission structure in terms of a modified Anderson Impurity Model [20,21]. 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. This controversy has spilled over into issues such as the volume collapse associated with the alpha to gamma phase transition [22-24] and the electronic structure of Ce compounds [25 - 28]. The model proposed by Gunnarsson and Schoenhammer [20,21] is a specific case of a more generalized picture in which the crucial element is the competition between the bandwidth (W) and correlation strength (U), as discussed by Kotliar and Vollhardt. [29] Considering the remaining uncertainty associated with the spectral features and valence electronic structure of Ce, it seemed plausible that the situation would benefit from the application of a spectroscopy with increased resolution and probing power. To this end, we have applied circularly polarized soft x-rays and true spin detection, in a modified form of the photoelectron spectroscopy experiment, to the enigmatic Ce system. The result of this is that we have observed the first experimental proof of spin shielding, the central tenet of the Gunnarsson-Schoenhammer model, using Fano Effect measurements.

The Fano Effect is the observation of spin specific photoelectron emission from the valence bands of a non-magnetic material due to excitation with circularly polarized light. First predicted in 1969 by Fano [30], the effect was experimentally confirmed by measuring the polarization of alkali vapor beams using detection of ions [31 - 33] and photoelectron emission [34] shortly thereafter. Subsequently, the effect was observed in the spin resolved photoemission of non-alkali systems, including the heavy atoms such as Th [35], Hg [36], and Xe/Pd (111) [37]. A variation of the Fano effect, in the core level photoemission of non-magnetic materials, has also been measured using both circular dichroism [38] and linear dichroism [39,40]. Our data for the Au4f states are shown in Reference 5.

The experiments were performed at the Advanced Light

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Source (ALS) at Lawrence Berkeley National Laboratory and the Advanced Photon Source (APS) at Argonne National Laboratory. Details of the instruments and experimental setups are described elsewhere. [4,5] However, the general principal of the experiment can be summarized as follows. By using a chiral probe, such as circularly polarized x-rays, for the excitation in conjunction with true spin detection, one is able to obtain a spin-sensitivity in NONMAGNETIC systems. The circularly polarized radiation establishes an axis of quantization that can be inverted by reversing the helicity of the circularly polarized radiation. In the same way that spectra in ferrro-magnetic systems are collected for both directions of macroscopic magnetization, data in the non-magnetic systems are collected for both circular polarizations, thus allowing for the determination and removal of instrumental asymmetries.

$$\text{Polarization }_{Circ} = P_C \propto \; [(I^{\uparrow}_{+} + I^{\downarrow}_{-})^{1/2} - (I^{\downarrow}_{+} + I^{\uparrow}_{-})^{1/2}] \; / \; [(I^{\uparrow}_{+} + I^{\downarrow}_{-})^{1/2} + (I^{\downarrow}_{+} + I^{\uparrow}_{-})^{1/2}] \quad \text{Eq 1.}$$

(Here the arrows denote spin and the +/- denote the excitation chiral arrangement.) Because of the short time structure for the x-ray absorption and photoemission event (10^{-15} sec – 10^{-18} sec), this measurement is potentially fast enough to probe the dynamic shielding hypothesized for electron correlated systems. Finally, the success of this method is predicated upon the presence of a spin-obit splitting and the predominance of localized effects in the electronic structure. Strong itinerancy would wash out the effects being sought by this measurement. Thus, observation of strong Fano dichroic effects have been made in the past for core levels in non-magnetic systems. [5, 38 – 40] The issue for Ce was simple: could this work for the valence states?

As can be seen in Figure 1, we have indeed observed Fano dichroic effects in the valence states of Ce polycrystalline films. In the top panel, data on the 4d to 4f resonance is shown. The advantage of being on resonance is the improvement of the counting rates owing to the larger cross-sections. The disadvantage is the somewhat increased complexity owing to the presence of the indirect channel of resonant photoemission along with the usual direct channel of regular photoemission. In this case, the additional complexity manifests itself in two ways: (1) a large static polarization associated with the the dominance of singlet coupling in the indirect channel decay path [Figure 2 and Ref. 4] and the presence of an additional strong sub-feature at a binding energy of 1 eV. [11,41] The solution for the first problem is simple: by subtracting off a constant polarization from the "raw" polarization shown in the third panel from the top in Figure 1, an adjusted polarization is obtained (shown in the second panel of Figure 1) and from the adjusted polarization and the

integrated spectrum, it is then possible to generate the spin resolved spectra shown in the top panel of Figure 1. Here it is clear that there is an underlying spin structure in the valence states of Ce. The second issue, the presence of the fairly strong sub-feature at 1 eV binding energy will be addressed in more detail below.

Furthermore, it is possible to observe similar effects in an off resonance experiment. In the lower half of Figure 1, results are shown for data collected in a chiral configuration, using unpolarized HeI radiation at an energy of 21.22 eV. Although conceptually more convoluted than the case using circular polarization, the data collected in this mode is essentially equivalent with that collected using circularly polarized x-rays. First, it has been established that under many conditions x-ray magnetic linear dichroism in photoelectron

spectroscopy provides essentially the same information as provided by x-ray magnetic circular dichroism in photoelectron spectroscopy. [42, 43] Second, because of the vectorially chiral selection rules for these processes, unpolarized radiation can produce the same effect, albeit with twice the background (and thus 1/2 of the percentage dichroism) relative to properly linearized polarization. [44] Unfortunately, because the chirality of this experiment is induced by the orientation of the Poynting vector of the incoming x-rays and the emission direction of the electrons relative to the perpendicularly aligned spin, chirality reversal is very difficult and requires an physical reconfiguration of the experimental apparatus. Thus, we chose to instead perform the experiment in one configuration and remove the instrumental asymmetry mathematically.

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

The static offset in the asymmetry (shown in the bottommost panel of Figure 1) has been subtracted from the "raw" polarization, to provide an adjusted polarization, shown in the panel second from the bottom. From this adjusted polarization and the integrated photoemission spectra, the spin resolved spectra in the panel third from the bottom have been generated. (Alternate forms of asymmetry removal were also pursued, each producing essentially the same result shown in Figure 1.) Again a significant spin polarization

of the Ce valence bands is observed, similar to but not quite identical with that of the data in the topmost panel of Figure 1.

Additional information regarding the nature of these states can be gleaned from spin integrated photoelectron spectroscopy. The data in Figure 2 demonstrates the strong f-character and bulk nature of both features. In the Ce 4f resonant photoemission, the increase in cross section is driven by the addition of an auxiliary channel involving either a 3d or 4d core level. Because of the

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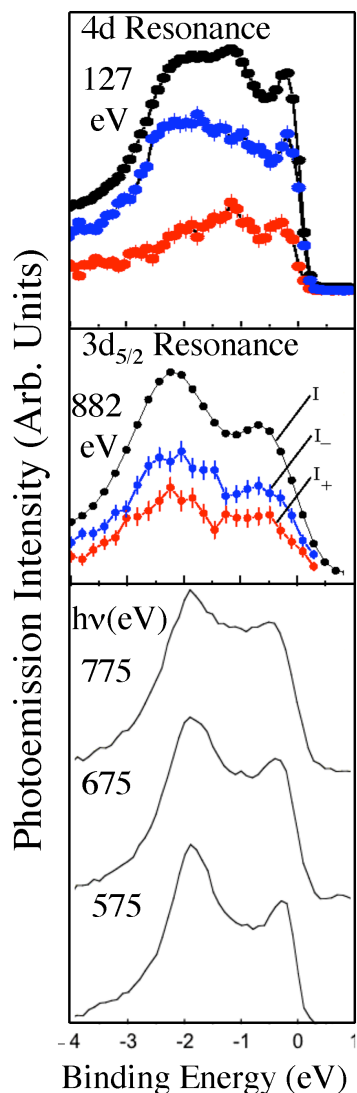

Figure 2
Top panel: Spin-resolved and spin-integrated spectra of polycrystalline Ce at the 4d to 4f resonance. Middle panel: Spin-resolved and spin-integrated spectra of polycrystalline Ce at the $3d_{5/2}$ resonance. Bottom panel: Spin-integrated spectra of polycrystalline Ce. The energy bandwidth was 0.32 eV at 575 eV, 0.43 eV at 675 eV and 0.56 eV at 775 eV. Thus the resolving power $(E/\Delta E)$ in each case was near 1500.
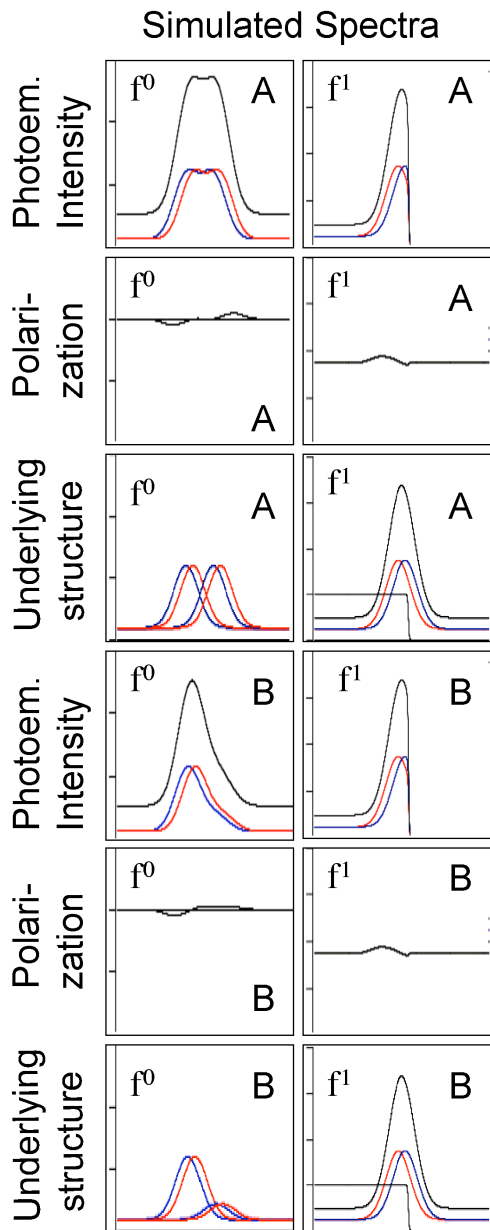

Figure 3
Spectral simulations for Case A and B, as described in the text.

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strong dipole selection rules, the amplification is f-state specific. Thus, the observation of enhancement of both the Fermi level feature and the higher binding energy feature in the 4d resonance and the 5d resonance indicates that both states have a strong and roughly equivalent degree of f-character. In the bottommost panel of Figure 2, a series of spectra at higher photon energies but below the 3d threshold are shown. Except for smearing of the features due to increasing energy bandwidth as the photon energy increases, the relative magnitudes of the two features remain fairly constant and consistent with that of the spin integrated spectra in Figure 1. Following the lead of Mo et al [3], this leads to the conclusion that both features are bulk derived. The importance of these two observations will become clear in the discussion which follows below.

From the utilization of simple spectral simulations, it is possible to gain significant insight into the nature of what is driving these observed spin polarizations, as illustrated in Figure 3. Here we have a fairly broad individual peak width with only a small spin-orbit splitting. In Case A, corresponding to the Resonant PES data at $h\nu$ = 127 eV, three sets of spin orbit split peaks are used. The pair near the Fermi Energy, with spin down leading spin up, is truncated by the Fermi function. The effect of this is to produce two peaks with essentially the same Fermi edge but different widths. The other two peaks, corresponding to the

symmetric and anti-symmetric states observed by D.V. Vyalikh et al [41], each have spin up leading spin down. This closely-spaced pair of sub-features combines to produce a broadened integrated peak and spin structure, with polarity reversed relative to the Fermi energy peak. In case B, corresponding to the off-resonance PES data at $h\nu$ = 21.22 eV, three sets of peaks are again used, but this time one of them is reduced in intensity relative to the other two. The same structure is observed near the Fermi energy as in Case A, but the higher binding energy feature is now more skewed and exhibits a more narrowly spaced polarization. Nevertheless, this polarization retains the reversed phase relative to the Fermi Level peak. Thus, the central observation here is that the there is a phase reversal between the spectral feature at the Fermi Level and that at higher binding energies.

The phase reversal, coupled with the previously demonstrated f-character of both features, is a direct proof of dynamical spin shielding in Ce. Phase reversals in dichroic studies have been observed before. [45, 46] However, in these previous studies some sort of net magnetization was present and the direction of the phase can be affected by the site symmetry and the orbital momentum parentage of the states. In the case of Ce, the situation is different. The similar parentage of both features, with a strong f-character contribution, means that there should be no phase reversal unless there is a spin

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counter-alignment. Moreover, these Fano effect measurements are dynamic. There is NO net magnetic vector in Ce. Thus the spin counter-alignment is exactly that hypothesized by Gunnarsson and Schoenhammer in 1983. [20,21] However, there is one inconsistency relative to the model of Gunnarsson and Schoenhammer, which assigned the 2 eV peak (f^0 or LHB) as being f derived and the peak at the Fermi energy (f^1 or Kondo) as being of valence band (spd) character. Nevertheless, a recent work by Antoine Georges [47] suggests that the same species can screen itself, in something like a Hubbard picture with only one type of electron species, within a Dynamical Mean Field Theory (DMFT) computational scheme. In his DMFT modeling of a Mott transition, he finds that "Electrons are itinerant in the metallic phase, and the moments are quenched. Within DMFT this quenching is akin to a (self-consistent) local Kondo effect." It may not be unreasonable to expect that a DMFT extension of the GS model would ultimately mix the states to the degree that they would seem to be of the same species, with both possessing significant f-character.

In summary, it has been demonstrated that (1) both spectral features in the valence bands of Ce are bulk derived and possessing significant f-character and (2) there is a dynamic spin counter alignment between the two features. These facts, taken together, confirm the original model of Gunnarsson and Shoenhammer, with the minor modification of state mixing between the two features. This study also illustrates the efficacy and potential of using the Fano Effect to probe spin correlation in nonmagnetic systems.

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