IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

An alternative model for electron correlation in Pu

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 422202

(http://iopscience.iop.org/0953-8984/20/42/422202)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 29/05/2010 at 15:58

Please note that terms and conditions apply.

IOP FTC

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 422202 (5pp) doi:10.1088/0953-8984/20/42/422202

FAST TRACK COMMUNICATION

An alternative model for electron correlation in Pu

S W Yu[1], **J G Tobin and P Söderlind**

Lawrence Livermore National Laboratory, LLNS-LLC, Livermore, CA, USA

E-mail: Yu21@LLNL.Gov

Received 30 July 2008, in final form 31 August 2008
Published 16 September 2008
Online at stacks.iop.org/JPhysCM/20/422202

Abstract

Using a density functional theory based approach that treats the 5f electrons relativistically, a Pu electronic structure with zero net magnetic moment is obtained, where the 5f orbital and 5f spin moments cancel each other. By combining the spin and orbital specific densities of states with state, spin and polarization specific transition moments, it is possible to reconstruct the experimentally observed photoemission spectra from Pu. Extrapolating to a spin-resolving Fano configuration, it is shown how this would resolve the extant controversy over Pu electronic structure.

(Some figures in this article are in colour only in the electronic version)

Despite substantial progress in the recent past and extended effort over many years [1], the exact nature of the electronic structure of Pu has not been resolved. While Pu is of immense technological and scientific importance and its phase diagram is a study in both complexity and far-reaching impacts from seemingly trivial variations, there still is no consensus regarding its electronic structure ([1–8], and references therein). There have been several different avenues of attack upon the problem, but each seems to be beset with its own limitations and inherent flaws. For example, by accepting substantial magnetic moments in Pu, it is possible to explain the geometrical structure of all six phases [2]. However, the vast body of experimental data indicates that there is no long range magnetic ordering in Pu [3]. To avoid this apparent contradiction, some researchers suggested that Pu had a 5f occupancy of nearly six, thus effectively filling the lower $5f_{5/2}$ sub-shell and diminishing the likelihood of a magnetic moment [4–6]. Unfortunately, this approach was also inconsistent with a substantial body of experimental evidence, with respect to the 5f occupancy. In this case, x-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) have been used to demonstrate the relativistic nature of the Pu 5f states and that the total 5f occupation was near to five [7]. (Unfortunately, the situation for Pu is complicated by experimental limitations. For example, there has not yet been any report of a magnetic form factor for δ-Pu, which could help extract the orbital and spin components from the total moment. This might be due to the fact that polarized neutrons and large single crystal samples are needed and have not been available for δ-Pu. It should also be noted that neutron scattering experiments of Pu present a particularly difficult avenue of attack, due to the propensity of Pu to undergo fission.) Most recently, Shim *et al* [8] argue that they can explain Pu electronic structure completely, using a dynamical mean-field theory (DMFT) approach in which the magnetic moments are screened by valence spd electrons. However, questions still remain concerning the nature of electron correlation in Pu.

In this communication, an alternative picture for electron correlation in Pu is proposed. Using a density functional theory (DFT) based approach [9] (figure 1) that treats the 5f electrons relativistically, a Pu electronic structure with zero net magnetic moment is arrived at by constraining the spin moment so that the spin and orbital moments exactly cancel each other. To test this hypothesis, a direct comparison was made to extant δ-Pu(Ga) photoelectron spectra. However, rather than simply comparing the calculations themselves to the PES spectra, a process fraught with many potential pitfalls and inaccuracies, the spin and orbital projected state densities were used to generate a simulated spectrum, which was then compared to the experimental results. It is shown that by combining

[1] Author to whom any correspondence should be addressed.

 © 2008 IOP Publishing Ltd Printed in the UK

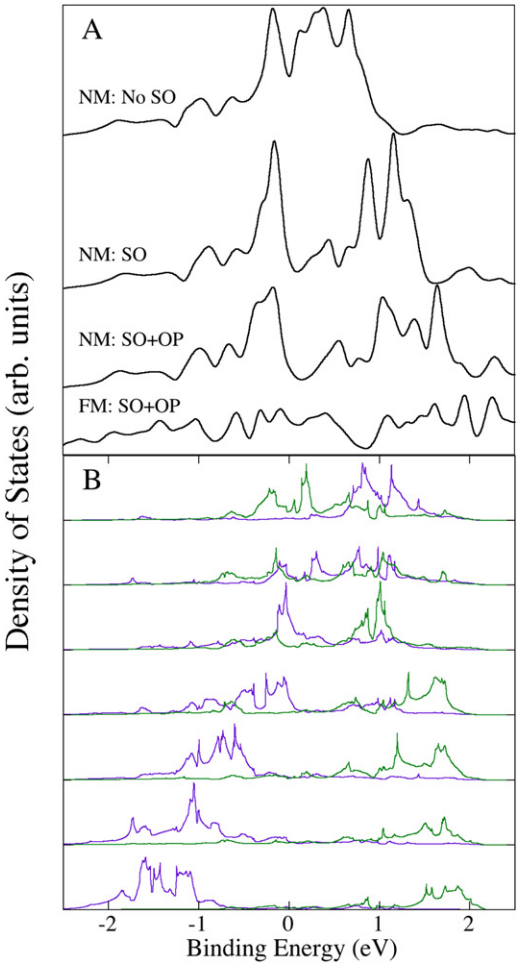

Figure 1. (A) Gaussian broadened (0.05 eV) total DOS, for several models: non-magnetic Pu without a spin–orbit splitting (NM:No SO); non-magnetic Pu with spin–orbit splitting (NM:SO); non-magnetic and ferromagnetic Pu with both spin–orbit splitting and orbital polarization (NM:SO + OP and FM:SO + OP). The (FM:SO + OP) model predicts a small net magnetic moment and is the starting point for the magnetic-cancellation approach. (B) Non-broadened 5f DOS. The m_l and m_s projected density of states from the magnetic-cancellation calculations. Spin up (down) is plotted in purple (green), with $m_l = 3$ at the top and $m_l = -3$ at the bottom.

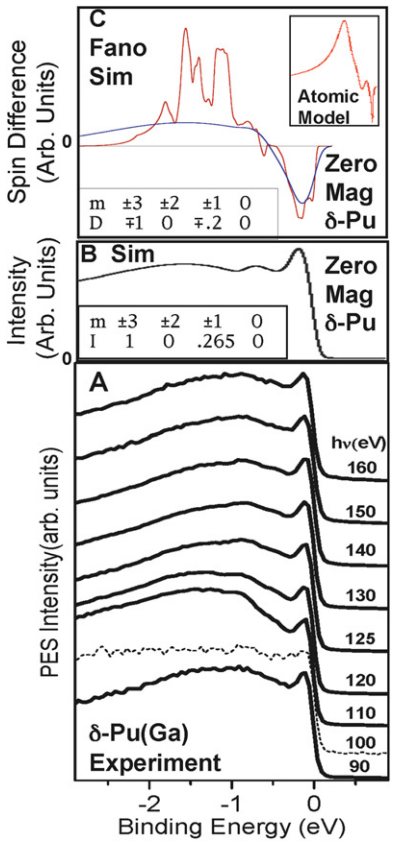

Figure 2. (A) The experimental PES results for δ-Pu(Ga), using linearly polarized x-rays as the excitation and with no spin detection. Each spectrum here was normalized to its most intense feature. See text for details. (B) A spectral simulation is shown here, for the zero-mag δ-Pu. See text for details. (C) The simulated Fano spectroscopy results for Pu are plotted here, based upon the magnetic-cancellation calculations. The blue (red) plot does (not) include lifetime broadening. The upper inset shows a previous result from a simplified atomic model [10]. See text for details.

the spin and orbital specific densities of states (DOS) with state, spin, and polarization specific transition moments [10], one can reconstruct the experimentally observed spectra from δ-Pu(Ga), obtained with linearly polarized soft x-rays [11], thus directly confirming the possibility of validity for this approach (figure 2). (This agreement is a necessary but not sufficient condition for the demonstration of the correctness of the model: for example, see [8]. The NM:SO model in figure 1(A) is known to be incompatible with PES [12], whereas the NM:SO + OP compares somewhat better with PES, but with a peak location farther from the Fermi level at -0.2 eV (not shown).) Furthermore, by extrapolating to a spin-resolving Fano experiment performed in a chiral configuration with a non-magnetic sample [10, 13, 14], it is predicted what the spectral response of Pu should be and how this would be different than that expected for a Kondo shielded system [13]. The spectral modelling for the extrapolation was tested using the non-magnetic and highly relativistic system Pt [14] (figure 3). It is proposed here that Fano measurements of Pu will permit the determination of the nature of electron correlation in Pu, because of the critical combination of high polarization and short time constant of the technique.

The theoretical electronic structure is obtained from an implementation of a full-potential linear muffin-tin orbital method (FPLMTO) [15]. The 'full potential' refers to the use of non-spherical contributions to the electron charge density and potential. This is accomplished by expanding these in cubic harmonics inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for the semi-core 6s, 6p, and valence 7s, 7p, 6d, and 5f states, these pairs are different. Spherical harmonic expansions are carried out through $l_{max} = 8$ for the bases, potential, and charge density. For the electron exchange and correlation energy functional, the generalized gradient approximation [16] is adopted. The details of the experimental data collection are described elsewhere [11].

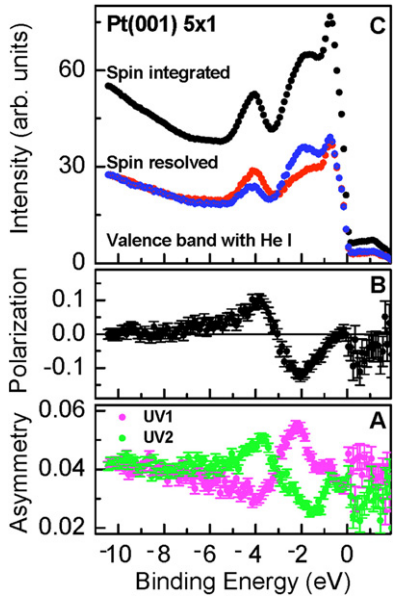

Figure 3. The Fano spectroscopy results for Pt. The electrons were collected along the sample normal. The He I radiation was incident from either the left or the right side, at an angle of 45°. The spin measured was perpendicular to the plane containing the He I radiation and the sample normal. (A) The asymmetries from the left and right He I sources, showing the spin reversal with chirality reversal. (B) The polarization. (C) The spin resolved and spin-integrated spectra, using unpolarized He I photons as the excitation. Spin up (down) is blue (red).

However, it should be noted that both the calculations and experiments face substantial difficulties. The calculations focus upon the 5f electronic states in which itinerancy, hybridization, spin–orbit splitting, and electron correlation interact complexly [2, 9]. The experiments are limited by the surface reactivity, complex phase diagram, toxicity and the highly radioactive nature of the material. The experimental data was collected from a young, purified sample of δ-Pu(Ga), where a small amount of Ga is used to stabilize the δ phase at room temperature [7, 11].

The calculations of the m_l and m_s specific DOS were made as follows. Including both spin–orbit splitting and orbital polarization [9] the variational principle of the DFT was applied to a magnetically ordered δ-Pu fcc lattice. The magnitude of the calculated orbital moment was about 90% of the spin moment and aligned anti-parallel. A perfect cancellation between spin and orbital magnetic moments was achieved for a 0.35 μ_B decrease of the spin moment (the calculated spin moment is about 3.35 μ_B and orbital moment is -2.95 μ_B) [9]. For this configuration, each and every δ-Pu is magnetically neutral, possessing neither long range magnetic ordering nor a permanent magnetic moment. The total DOS from the cancellation model is not shown but very similar to FM calculation with a small net moment displayed in figure 1(A) (FM:SO + OP). Notice that both spin–orbit (SO) and orbital polarization (OP) has a significant influence on the DOS also when the spin is zero (NM:SO + OP) [9]. The m_l and m_s projected DOS (cancellation model) is shown in figure 1(B). It should be emphasized that the perfect spin and orbital cancellation is obtained by construction, by decreasing the spin moment to account for the possibility that it is somewhat overestimated by the theory. The spin moments are usually overestimated in magnetic actinide systems. For instance, in uranium pnictide systems [17] DFT, with the commonly used electron exchange and correlation approximations, overestimates the U spin moment by an average of about 0.7 μ_B.

Next, it is necessary to convert the m_l and m_s specific density of states into a simulated spectrum. To do this, the transition moments for each m_l and m_s state must be generated for the geometry relevant to the photoelectron spectroscopy experiment. In this case, the excitation was linearly polarized (p-polarized) x-rays, incident at an angle of 60° relative to the sample normal, with the polarization in the plane containing the incoming photons and the sample normal. The photoelectrons were collected along the sample normal. Using this geometry and a plane-wave-like final state, one can demonstrate that the state specific transition moments or intensities are those shown in the inset of figure 2(B) [10]. While the overall absolute intensity is photon energy dependent via the radial matrix elements, the relative intensities within the 5f manifold are merely dependent upon the spherical harmonics involved. The first step in generating the simulated spectrum is to calculate the properly weighted contributions from each specific m_l, m_s state. Thus, by truncating the m_l and m_s DOS (figure 1(B)) at the Fermi energy (only occupied states can emit) and multiplying by the transition moments shown in figure 2(B) and summing, one arrives at the first approximation to the oscillatory part of the simulated spectrum, which is due to the elastic spectral features. However, two more important operations must be carried out: (1) proper instrumental and lifetime broadening, and (2) the inclusion of an appropriate spectral background. To be consistent with past work, the process suggested by Arko *et al* [18] was followed, including the utilization of a Shirley background function [19]. The only adjustable parameter is a solitary background-scaling factor, which was chosen to optimize the agreement with the experimental data. Finally, the simulated spectrum was obtained by summing the properly broadened elastic features and the Shirley background. The result is shown in figure 2(B). Again, it should be noted that the transition moments used are not based on matrix elements obtained with Kohn–Sham states, but rely on model assumptions. This simple model of dichroic, spin specific transitions has been demonstrated to work well with a number of systems ([10, 13] and references therein).

Before going on to a comparison with experimental data, a brief discussion of the photoelectron spectra is warranted. The data shown in the figure 2(A) cover the photon energy range of $h\nu = 90$–160 eV. This photon energy range includes the resonant regime connected with the Pu 5d core level. In resonant photoemission, a secondary 5f channel opens up through the 5d core level, which can interfere with the direct 5f photoemission process. On resonance ($h\nu = 110$–140 eV), the interference is constructive. At anti-resonance ($h\nu = 100$ eV), the interference is destructive. Because of the strong electric dipole selection rules, resonant photoemission is a powerful test of f character of the spectral features. As can be seen from

the spectra at $h\nu = 110$–140 eV in figure 2(A), the spectral features of interest are clearly 5f derived. Moreover, all of the spectra (with the exception of that at the anti-resonance at $h\nu = 100$ eV) have essentially the same appearance: a peak at the Fermi energy, with a minimum near the binding energy of $-1/2$ eV and a broad maximum in the binding energy range of about -1 to -2 eV. This includes the spectra from below resonance ($h\nu = 90$ eV), on resonance ($h\nu = 110$–140 eV) and above resonance ($h\nu = 150$ and 160 eV). Thus we are very confident that these features are 5f derived and representative of the 5f spectral shape. (For a more extensive discussion of Pu resonant photoemission, the reader is directed to [11].)

Comparing the simulated spectrum from the magnetic-cancellation model (figure 2(B)) to the experimental spectra shown in figure 2(A), it is clear that the simulated spectrum reconstructs the key features of the experimental data: the narrow maximum near the Fermi energy, the minimum near $-1/2$ eV binding energy and the broad maximum near -1 to -2 eV. There does seem to be a small dip in the simulation, near BE $= -1$ eV, that does not appear clearly in the experiment. This is not unexpected: real samples are imperfect, with various sources of inhomogeneous broadening. Small nuances such as this are often lost between theory and experiment. Finally, it should be noted that the results shown in figure 2(B) are for a final state g-wave, which should dominate at these photon energies. Similar results can be obtained with a d-wave final state [10].

Given the success of this method and the success of the previously reported DMFT approach [8], the question then becomes the following. Is there another level of information that will allow us to differentiate between these two hypothesized solutions? We believe there is and suggest that Fano measurements are the key to accessing this additional level of information.

Fano spectroscopy [20] is the measurement of spin resolved effects in non-magnetic systems. It has recently been utilized to confirm the dynamically anti-parallel alignment of quasi-particle (Kondo) and f-state (lower Hubbard band) electrons in Ce [13]. In figure 3, the results for the strongly relativistic 5d Pt system are shown [14]. Specifically, in figure 3(A), we show the asymmetries (A) for the two experimental configurations, one with the source to the left and the other with the source to the right.

$$A = \{c(\mathrm{up}) - c(\mathrm{dn})\}/\{c(\mathrm{up}) + c(\mathrm{dn})\}. \qquad (1)$$

Here, c is counts, up or down (dn). The reversal of the spin dependency with the change in source confirms the Fano nature of these spin effects. From these asymmetries, one can generate a polarization (figure 3(B)) and spin resolved spectra (figure 3(C)), as described in [14]. The large spin–orbit splitting in the Pt 5d states drives this spin dependence, which does not require a permanent magnetic moment nor long range magnetic ordering. If it is possible to see such an effect in the relativistic Pt 5d states, why not in the relativistic Pu 5f states?

The results of the simulation of the Pu Fano spectroscopy are shown in figure 2(C). This is potentially the result for either a measurement with circularly polarized x-rays, where the measured spins are co-aligned with the helicity, or an experiment like that shown for Pt in figure 3, where the spin measured is perpendicular to the reaction plane and the chirality is derived from the orientation of the experimental vectors [13, 14]. Here, the dichroic intensities shown in the inset in figure 2(C) are used along with the m_l and m_s specific density of states shown in figure 1(B). Two broadening cases have been included: instrumental broadening with (blue) and without (red) lifetime broadening, following the procedure described above for the spin-integrated spectrum in figure 2(B). However, for the spin difference, a Shirley background has not been utilized. It is expected that the backgrounds will tend to cancel each other in the subtraction process. The product of this process is shown in figure 2(C). Interestingly, there is a qualitative agreement with the result predicted using an atomic model of Pu [10], shown in the inset of figure 2(C). Moreover, these simulated spectra are very different than that observed for Ce [13], a known Kondo system. In the case of the Ce system, there is also spin reversal between the state at higher binding energy (the lower Hubbard band feature) and the state near the Fermi energy (the quasi-particle or Kondo feature). However, there is a major difference between the Ce and Pu results. In the Fano simulation for Pu, the higher binding energy peak and the Fermi energy peak are each monotonically of one type of spin, but reversed relative to each other. In the Ce system, each of the higher binding energy and Fermi energy peaks are split, composed of both spin up and spin down, but the phases are reversed. In the Ce Fermi energy peak, down leads up, and in the higher binding energy peak, up leads down. Thus, this experiment should provide the detailed information necessary to distinguish between the two proposed models for electron correlation in Pu.

An alternative model for electron correlation in Pu has been proposed and it has been demonstrated that it is consistent with the experimental PES results. A new experiment (Fano spectroscopy) is proposed to resolve the Pu electronic structure controversy conclusively.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the US Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. Work that was performed by LLNL personnel was supported in part by the Office of Basic Energy Science at the US Department of Energy.

References

[1] Johansson B 1975 *Phys. Rev.* B **11** 2740
Skriver H L, Andersen O K and Johansson B 1978 *Phys. Rev. Lett.* **41** 42
[2] Söderlind P 2001 *Europhys. Lett.* **55** 525
Söderlind P, Landa A and Sadigh B 2002 *Phys. Rev.* B **66** 205109
Söderlind P and Sadigh B 2004 *Phys. Rev. Lett.* **92** 185702
[3] Lashley J C *et al* 2005 *Phys. Rev.* B **72** 054416
[4] Pourovskii L V *et al* 2006 *Europhys. Lett.* **74** 479
[5] Shorikov A O *et al* 2005 *Phys. Rev.* B **72** 024458
[6] Shick A B, Drchal V and Havela L 2005 *Europhys. Lett.* **69** 588

[7] Tobin J G *et al* 2005 *Phys. Rev.* B **72** 085109
van der Laan G *et al* 2004 *Phys. Rev. Lett.* **93** 097401
Moore K T *et al* 2003 *Phys. Rev. Lett.* **90** 196404
[8] Shim J H, Haule K and Kotliar G 2007 *Nature* **446** 513
[9] Söderlind P 2007 *J. Alloys Compounds* **444/445** 93
Söderlind P 2008 *Phys. Rev.* B **77** 085101
[10] Tobin J G 2007 *J. Alloys Compounds* **444/445** 154
[11] Tobin J G *et al* 2003 *Phys. Rev.* B **68** 155109
[12] Wills J M *et al* 2004 *J. Electron Spectrosc. Relat. Phenom.* **135** 163
[13] Tobin J G *et al* 2007 *Europhys. Lett.* **77** 17004
[14] Yu S-W and Tobin J G 2007 *Surf. Sci.* **601** L127
[15] Wills J M *et al* 1998 *Electronic Structure and Physical Properties of Solids* ed H Dreysse (Berlin: Springer) p 148
[16] Perdew J P *et al* 1992 *Phys. Rev.* B **46** 6671
[17] Wisniewski P *et al* 1999 *Phys. Rev.* B **60** 6242
[18] Arko A J *et al* 2000 *Phys. Rev.* B **62** 1773
[19] Shirley D A 1972 *Phys. Rev.* B **5** 4709
[20] Fano U 1969 *Phys. Rev.* **178** 131
Fano U 1969 *Phys. Rev.* **184** 250