Pu Electronic Structure and Photoelectron Spectroscopy

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Abstract. The electronic structure of PuCoGa₅, Pu metal, and PuO₂ is explored using photoelectron spectroscopy. Ground state electronic properties are inferred from temperature dependent photoemission near the Fermi energy for Pu metal. Angle-resolved photoemission details the energy vs. crystal momentum landscape near the Fermi energy for PuCoGa₅ which shows significant dispersion in the quasiparticle peak near the Fermi energy. For the Mott insulators AnO₂ (An = U, Pu) the photoemission results are compared against hybrid functional calculations and the model prediction of a crossover from ionic to covalent bonding is found to be reasonable.

1. Introduction

The properties of Pu materials are defined in large part by the 5f electrons which are at the boundary between localized and itinerant character. In the actinide elements, Pu is the transition point for the 5f electrons moving from bonding character in the lighter actinides (Np and lower) to localized character in the heavier actinides (Am and higher). Moreover, this crossover point in 5f character at Pu in the actinide elements is also found in many Pu compounds as well. The three materials δ-Pu metal, PuCoGa₅, and PuO₂ serve as examples. In Pu metal there are six solid state allotropes with a 21% volume change between the alpha and delta phases. The 5f character shifts from more itinerant in the high density alpha phase toward a more localized character in the lower density delta phase. [1, 2] The 18.5 K superconductor PuCoGa₅ [3] has a Tc an order of magnitude higher than its Ce counterparts while UCoGa₅ shows no evidence of strongly correlated electron characteristics, properties again pointing toward the degree of interaction for the f-electrons in bonding. Within the Mott insulator family of actinide dioxide, [4] there is a crossover between ionic and covalent bonding at PuO₂. Central to the understanding of these electronic structure properties is an accurate picture for the characteristics of Pu 5f electrons. Photoelectron spectroscopy (PES) in various forms including temperature dependent PES and angle-resolved photoemission (ARPES) is used along with advanced computational methods to determine the electronic structure of these complex Pu materials.

Due to the aforementioned crossover point in 5f character, a full range of Pu materials and associated 5f characteristics may be observed covering localized 5fs in PuTe [5] and PuSb [6] to rather itinerant 5fs in α-Pu [2]. The Pu materials presented below δ-Pu, PuCoGa₅, and PuO₂ show a somewhat intermediate 5f character and experimental signatures associated with hybridized electronic structure. For single crystal PuCoGa₅, the appearance of periodic and dispersive 5f states provides compelling evidence that there is a strong component of itinerant character to the electronic structure.
near the Fermi energy. In δ-Pu, the binding energy, lineshape, and temperature dependence of the spectral feature at the Fermi energy help determine the ground state electronic properties.

2. Results

Photoemission data were collected using the Laser Plasma Light Source taking advantage of the high energy resolution available from the He lamp combined with a low temperature capability. The Pu metal samples were polycrystalline, Ga stabilized, δ- (fcc) phase. In Figure 1a, the energy resolution is 35 meV, at a photon energy of 40.8 eV and a sample temperature of 15 K. The energy resolution and position were determined by a Cu Fermi level reference spectrum. In Figure 1b, the resolution is relaxed to 60 meV in order to collect data at two temperatures before any significant sample deterioration occurs.

Photoemission data for δ-Pu is show in Figure 1a with two important details; 1) the lineshape of the spectral feature may be described as a symmetric oscillator function cut by the low temperature Fermi function, 2) the position of the Fermi energy high on the spectral feature indicates the energy position of the peak is at or very near the Fermi energy and that this is a ground state energy position. In the b) and c) frames of Figure 1, the temperature dependence of the PES data and a simple model for a narrow peak are presented. In the b) frame, we show the PES data taken at 77 and 300K. While there is a significant change with temperature in the PES data, the c) frame shows a simple model for temperature dependence that is consistent with the PES data based on a Lorentzian lineshape 200 meV in width at the Fermi energy. The model temperature dependence illustrates the role of the Fermi function acting on a ground state feature. Combining this Pu high resolution and temperature dependent data with previously published photon energy dependence [7] makes a strong case that the peak at the Fermi energy is a narrow band, of mixed 5f-conduction band character, centered at or very near the Fermi energy in the ground state of δ-Pu.

![Figure 1. a) High resolution PES for δ-Pu with 35 meV energy resolution at a temperature of 15 K, b) temperature dependence of Pu PES between 77 and 300 K, c) simulation of temperature dependence for a narrow peak at the Fermi energy as a function of temperature (77 and 300 K after b) ).](image)

ARPES data for PuCoGa$_5$ is presented in Figure 2. The original photoemission research on single crystal, flux grown samples [8] cleaned by laser ablation showed a narrow peak at the Fermi energy consistent with both the modest enhanced mass value for PuCoGa$_5$ as well as a range of other Pu materials showing both a localized feature well below the Fermi energy, and a hybridized 5f feature at the Fermi energy. In Figure 2, we present ARPES data for single crystal PuCoGa$_5$, cleaved at 10K to expose a clean, stoichiometric surface. The results from the new, cleaved single crystal data are consistent with the original single crystal results. The new data presented in Figure 2, show clear evidence of a dispersive peak, with some Pu 5f character, moving through the Fermi energy.
Figure 2. a) Angle-resolved PES for PuCoGa$_5$ at $h\nu=21.2$ eV showing 120 meV near the Fermi energy (dotted black line) in the horizontal plane and 18 degrees of angle in the vertical plane. The 18 degrees of angle corresponds to 90% of the crystal momentum space along $\Gamma$-X using 10 eV for the inner potential. Color represents relative intensity. b) Energy distribution curves at four different angles showing the dispersion of the peak through the Fermi level.

The position in reciprocal space for the ARPES data was assigned by comparison to both UCoGa$_5$ and CeCoIn$_5$ data and their associated inner potentials, then projecting an averaged inner potential of 10 eV for PuCoGa$_5$. With a 10 eV inner potential and a photon energy of 21.2 eV, one may calculate the reciprocal lattice location to be just below a $\Gamma$-point in the $\Gamma$-Z direction. Transforming angles into crystal momentum at this energy shows the in-plane $\Gamma$-X direction requires about 20 degrees of angular acceptance to cover the zone center to edge. We use angles in degrees rather than reciprocal lattice dimensions in figure 2 since the inner potential is estimated by comparison to known, closely related materials rather than experimentally determined. Comparing to the original photoemission on PuCoGa$_5$ [8], the linewidth of this peak near the Fermi energy is less than 100 meV and the dispersion is at least 50 meV within the portion of reciprocal space defined by Figure 2. This is consistent with the reported linewidth and energy position, as the original data was angle-integrated PES, which would be a superposition of the narrower but dispersive peaks in the ARPES data set.

For the AnO$_2$ family of materials, the competition between kinetic energy and onsite Coulomb repulsion leads to Mott insulating character. To accommodate the competition between kinetic energy and Coulomb repulsion the hybrid functional model is applied to the AnO$_2$ family. [4,9] The hybrid functional predicted UO$_2$ as an ionic solid with small orbital character overlap between the O 2p and the U 5f levels. The energy separation of the 5f and 2p bands was observed experimentally by ARPES and a small amount of 5f-2p intermixing was observed in the U 5f levels as 200 meV of dispersion when the U-U interatomic separation would preclude any wavefunction overlap.[10]
Figure 3. PES and hybrid functional calculations for UO$_2$ and PuO$_2$. The left frames show the PES (blue) plotted against the calculations (red - adjusted for lifetime and instrument resolution). The right frames show the orbital (p, d, f) character for U, Pu and O within the model calculations. The agreement between PES and the calculation is good for both UO$_2$ and PuO$_2$, showing the separation between U 5f and O 2p states in the top frames and the hybridization between Pu 5f and O 2p states in the bottom frames. The energetic overlap in states for PuO$_2$ leads to the covalent bonding whereas the separation into two manifolds of states in UO$_2$ results in primarily ionic bonding.

In Figure 3 we show the hybrid functional calculations for UO$_2$ and PuO$_2$ compared with the PES data. The hybrid functional calculations predicted that for PuO$_2$, the separation between the O 2p levels and the Pu 5f levels would be eliminated leading to strong hybridization and thus a significant amount of covalency in PuO$_2$ whereas UO$_2$ had clear ionic character. In order to quantify the covalent character of PuO$_2$, recent ARPES data has demonstrated the strong intermixing between Pu 5f and O 2p levels. [11] The combination of the ARPES in references 10 and 11 with the angle-integrated photoemission in Figure 3 provides strong evidence for hybridization in PuO$_2$. Similarly, the UO$_2$ data is consistent with limited hybridization and energetically separated regions of 5f and 2p character. The photoemission results thus support the predictions of the hybrid functional model for the AnO$_2$ family of materials, which show strong mixing of the Pu 5f and O 2p states, a few eV below the Fermi energy. The systematic trend in the AnO$_2$ series showing convergence of the O 2p levels and the actinide 5f levels as the series moves from Th, U, Np to Pu is completely consistent with the PES results shown here for UO$_2$ and PuO$_2$.

For the metals $\delta$-Pu and PuCoGa$_5$, the first peak in the photoemission data is associated with a 5f-conduction state hybridized bulk feature. The identification of this peak as a bulk electronic structure feature rather than surface state is based on; 1) comparison to several different Pu materials all showing similar spectral features ($\delta$-Pu, PuCoGa$_5$, Pu$_2$RhGa$_8$, PuIn$_3$, PuSb$_2$), 2) the photon energy dependence of the peak [1], and 3) the observation of sample degradation with vacuum contaminants. These three points argue for a bulk electronic structure feature, the possibility of a minor component in this spectral feature which could be associated with a surface feature is open to future research. Additional experiments using normal emission ARPES and controlled dosing of adsorbates would enhance the points of differentiation between bulk vs. surface.

3. Summary

Both of the strongly correlated metals, $\delta$-Pu and PuCoGa$_5$ show two regions of 5f character, one near the Fermi energy and one removed by 1 eV or more from the Fermi energy. These two regions have been associated with hybridized Pu 5f character and localized Pu 5f character respectively. Temperature dependent and high resolution PES data for $\delta$-Pu metal give strong evidence that there is a narrow spectral feature centered very near the Fermi energy in the ground state. The position of the Fermi level high on the peak further supports the premise of a narrow feature at the Fermi energy. In the case of PuCoGa$_5$, the ARPES data provides direct experimental evidence that this first peak near
the Fermi energy is a dispersive quasiparticle state which moves through the Fermi energy as a function of crystal momentum. The PuCoGa$_5$ data show a peak less than 100 meV in width and dispersing at least 50 meV. For PuCoGa$_5$, direct observation of a dispersive peak in the ARPES data demonstrates the significant role of the periodic potential in understanding the electronic structure. For the AnO$_2$ Mott insulators, PES results show limited but non-zero wavefunction intermixing for the U 5f and O 2p states while there was strong hybridization between the Pu 5f and the O 2p levels consistent with the prediction of ionic bonding in UO$_2$ with covalent bonding for PuO$_2$. Overall, a combination of ARPES results and temperature dependent PES in addition to conventional PES provides insight on the electronic structure and ground state properties for a range of Pu materials from strongly correlated metals to Mott insulators.

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References
[1] J.M. Wills, et al., J. Elect. Spectr. and Related Phenom. 135, 163 (2004).
[2] A.J. Arko, et al., Phys. Rev. B 62, 1773 (2000).
[3] J.L. Sarrao, et al., Nature 420, 297 (2002).
[4] I.D. Prodan, et al., Phys. Rev. B 76, 33101 (2007).
[5] T. Durakiewicz, et al., Phys. Rev. B 70, 205103 (2004).
[6] T. Gouder et al., Phys. Rev. Lett. 84, 3378 (2000).
[7] J.J. Joyce, et al., Mat. Res. Soc. Symp. Proc. 986, 35 (2007).
[8] Joyce, et al., Phys. Rev. Lett. 91, 176401 (2003).
[9] I.D. Prodan, et al., Phys. Rev. B 73, 045104 (2006).
[10] L.E. Roy, et al., J. of Computational Chemistry, 29 (13), 2288 (2008).
[11] J.J. Joyce, et al., Mat. Res. Soc. Symp. Proc. accepted (2010).