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Resolving the Pu electronic structure enigma: Past lessons and future directions

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ABSTRACT

The nature and limitations of the photoelectron spectroscopy (PES) of Pu is discussed, particularly the absence of detailed fine structure. A novel experiment, Fano Spectroscopy, is suggested as a means to obtain additional fine structure, with which to bench-mark and differentiate theoretical models.

1. Discussion

The nature of the 5f electronic structure of plutonium (Pu) remains unclear [1]. Despite many recent attempts to resolve the issue, a plethora of important unanswered questions remain. While many theoretical approaches to the problem have been promulgated, the real source of the difficulty is the absence of sufficient experimental benchmarking. This paucity of impact on the part of experimental results is driven in part by the difficulties of working with Pu: it is highly radioactive, biologically toxic, chemically reactive and restricted in its distribution and permitted access to user facilities. The results of these liabilities include the following: (1) it is very difficult, if not impossible; to get large single crystals of single phase samples and; (2) many state of the art experiments can not be done because general user facilities are not available for use with Pu samples. Additionally, there is the apparently bizarre nature of Pu, which seems to defeat the efforts to analyze it. A wonderful example of this is the absence of detailed and variant fine structure in many of the spectroscopic investigations of Pu.

Consider the case of Photoelectron Spectroscopy (PES) of Pu. The low energy PES spectra of Pu have been available for a number of years [2]. These are often called VUV spectra, for 'vacuum ultra violet' and are associated with low energy excitations such as HeI at 21.22 eV and HeII at 40.8 eV. As shown in Fig. 1, there are some differences between the low energy valence band spectra of alpha-Pu and delta-Pu. These are well known, but to briefly summarize, the alpha-Pu has a triangular shape and the delta-Pu has a peak at the Fermi Energy (0 eV), followed by a minimum and then a broad maximum, possibly containing fine structure. In fact, in the high resolution spectra of Naegele in Fig. 1(B), it is possible to see the three peak spectral structure discussed by Gouder et al. [3]. These delta-Pu spectra are also consistent with the measurements of Arko et al. [4]. Unfortunately, going to the higher energies with an in-house laboratory X-ray source, such as a Mg Kα line at hν = 1254 eV or Al Kα line at hν = 1487 eV, causes the spectra to broaden, as shown in Fig. 1(A), rendering a the X-ray photoelectron spectra (XPS) of alpha-Pu and delta-Pu essentially indistinguishable [2,5,6]. Additionally, for each specific phase, alpha or delta, and He excitation, the features in the spectra are essentially constant and independent of photon energy. Thus there isn't any real difference between the HeI and HeII spectra, except perhaps for cross section effects [7]. It was hoped, that by going to synchrotron radiation and utilizing both different energies and high resolution, it might be possible to see more varied fine structure [1,8]. Unfortunately, this is not the case, as can be seen in Fig. 1(C). Here the spectra at the Cooper Minimum [1,7,8] (hν = 225 eV), off-resonance (hν = 180 eV) and on resonance (hν = 125 eV) are all essentially the same, with delta Pu signature of a peak at the Fermi Energy, a minimum and a broad maximum. (On resonance, the 5f character of the valence bands should be emphasized. Thus, the constancy of these features confirms the earlier assignment of the spectral features as being due to 5f electronic structure [1,8,9].) Even the anti-resonance spectrum (hν = 100 eV), which should emphasize the non-5f aspects of the valence band, has a remnant of this spectral structure. In fact, the strongest variant spectral structure is associated with the aging of delta-Pu and is only observed as an intensity variation manifested on resonance and as function of photon energy [8,9]. Because these photon energy dependent resonance experiments can only be performed with synchrotron radiation, this observation has proved to be of limited utility.

Similar results are observed in the core level spectra of Pu, as can be seen in Fig. 2. In Fig. 2(A), the 4f core levels of alpha-Pu

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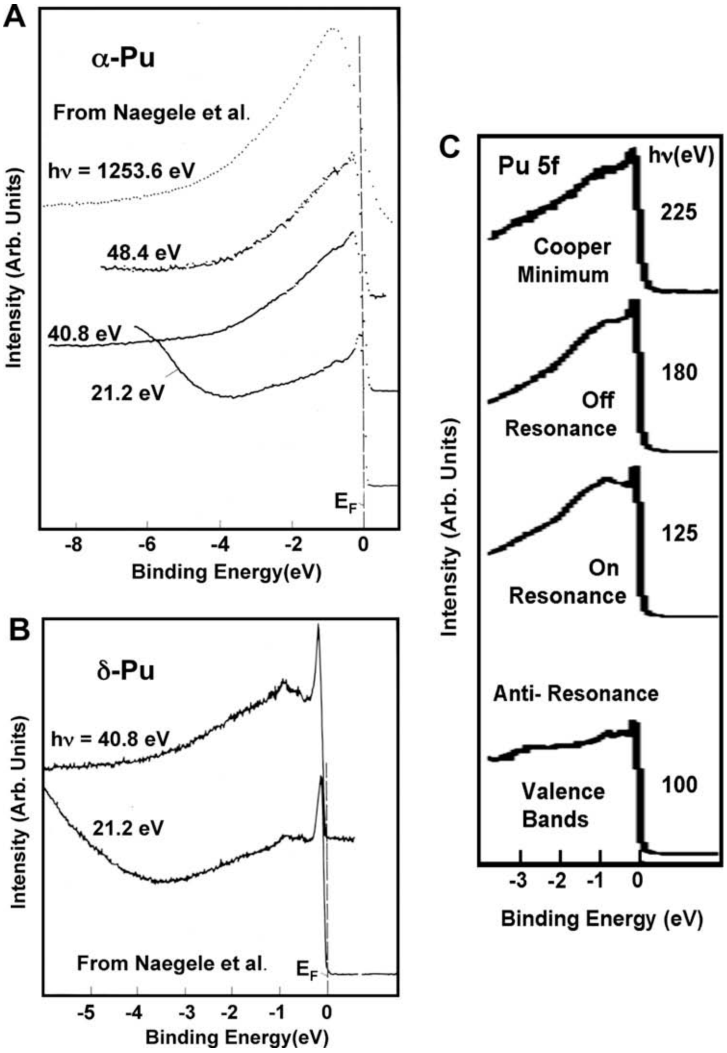

Fig. 1. Here are shown the valence band photoelectron spectra of alpha and delta Pu. (A) Photoelectron spectra of alpha-Pu, using He lamp excitation at 21.2 eV, 40.8 eV, and 48.4 eV and Mg Kα excitation (1253.6 eV). E_F is the Fermi Energy at a binding energy of 0 eV. Note the strong similarity of the spectra at low energies. The topmost spectrum in Fig. 1A illustrates a key point: whether using Al Kα (1487 eV) or MgKα (1254 eV) and alpha- or delta-Pu, the valence band fine structure is lost in the broadening of the Fermi edge and main features near the Fermi Energy. (B) Photoelectron spectra of delta Pu, using He I (21.2 eV) and HeII (40.8 eV). Again, note the strong similarity of the spectra. (C) Photoelectron spectra of Pu, with a delta-like reconstruction in the surface region of an alpha sample. From Tobin et al. [1]. The spectra in Fig. 1A and B are from Neagale, [2] and references therein. Additional spectra can be found in Baptist et al. [5] and Courteix et al. [6].

and delta-Pu, collected using synchrotron radiation at hν = 850 eV, are shown. Here, both samples exhibit a sharp feature followed by a broad feature, for each member of the spin-orbit split doublet. The delta-Pu spectrum has a relatively larger broad following feature, when compared with the alpha-Pu spectrum. These synchrotron radiation results mirror what was observed earlier using X-ray tube excitation, as shown in Insets A and B [2]. While this result provides a convenient means of distinguishing the phase in Pu samples, it provides little if any potential for further analysis, owing to the intrinsic, lifetime-driven, line-width of the spectra. Similar and enhanced problems are encountered in X-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) [1,10], as shown in Fig. 2(B). Both the 4d XAS and 5d XAS exhibit an intrinsic lifetime broadening of several eV. Cross sectional variations can be observed between different elements, as illustrated for U and Pu in Fig. 2(B). For the case of Pu, unfortunately, the 4d spectra for alpha-Pu and delta-Pu are essentially identical [1]. Similarly, neither aging nor oxidation produces much observable variation, possibly being masked by the large lifetime broadening. In fact, it can be argued on the basis of error analysis [11] that all Pu XAS/EELS 4d spectra are statistically indistinguishable [1]. In the case of the 5d spectra, as shown in the inset in Fig. 2(B), only a small relative intensity variation occurs with phase [1]. As in the case of the Pu 4f PES, while this result provides a convenient means of differentiating alpha from delta, there is not sufficient spectral structure to provide a basis for further investigations.

The results beg the question: how can additional spectral fine structure be obtained, in order to provide the experimental benchmarking of the various models of Pu electronic structure?

One possibility is angle resolved photoelectron spectroscopy (ARPES) as a probe of valence band dispersion within the Brillioun Zone of reciprocal space. For many materials, this has proven to be a strong test of the electronic structure [12]. In fact, recent studies of U valence band structure have been successfully carried out [13]. Unfortunately, the situation for Pu is significantly more difficult than U, for the following reasons. First, there is the issue of the effective absence of single crystals of Pu. Second, in general, Pu is far more radioactive and hazardous than U. Third, there is evidence that Pu is far more localized than U [3,4,10]. Thus, the dispersion will be significantly smaller and more difficult to observe, if it is there at all. Thus, it is proposed here to attack the problem in a different fashion.

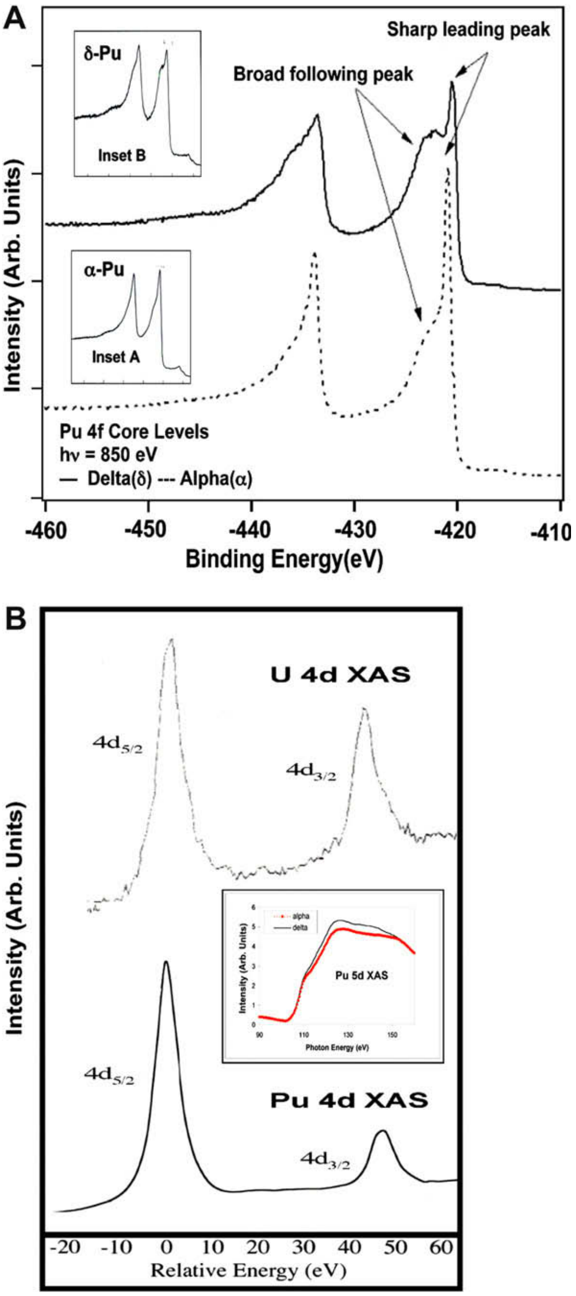

Fig. 2. The core level spectra of Pu, both photoelectron and X-ray absorption spectroscopy, are shown here. (A) Here are shown 4f core level photoelectron spectra of alpha and delta Pu, using synchrotron radiation at 850 eV. Both alpha and delta peaks are composed of two features: a sharp leading peak and a broad following peak. The alpha and delta spectra differ mainly in terms of the relative magnitudes of the leading and following peaks. Note the strong similarity of these spectra to those collected years earlier (Insets A and B) using Al Kα radiation (1487 eV), from Neagale, [2]. (B) The X-ray absorption spectra of Pu are shown here, from Tobin et al. [1]. The 4d spectrum is from an alpha Pu sample: note the significant change in branching ratio [$B = I_{5/2}/(I_{5/2} + I_{3/2})$], relative to the result for U. While this ratio varies significantly between actinide elements, for Pu the result is fairly independent of chemical or physical state. Within reasonable error analysis, alpha and delta, young and old, all have essentially identical XAS/EELS spectra. [Tobin et al. [1] and references therein.] It is even questionable whether this measurement can distinguish between metallic and oxidized Pu. Another example of this constancy can be seen in the inset, where there is a strong similarity between the 5d XAS of alpha and delta Pu. A limitation of the Pu XAS/EELS measurements is the lifetime broadening. The width of the features in the spectra in Fig. 2B is intrinsic and cannot be removed, being driven by lifetime broadening. The instrumental contribution in the Pu XAS measurements was 0.1 eV, which is insignificant when compared to the observed line-widths.

Recent experiments upon Ce [14] and Pt [15] each indicate the utility of using the Fano effect as a way to provide additional spectral structure in Pu [16]. In Fano Spectroscopy, a spin resolved PES [17,18] experiment is performed upon a 'non-magnetic' sample using chirally polarized excitation. In the case of Ce, the fundamental hypothesis of the Kondo-like models has been confirmed: the dynamic anti-alignment of the spins of the electrons of the lower Hubbard bands and the quasi-particle states. Interestingly, Ce is the 4f analog of Pu, with the transition between localized and delocalized behavior being centered upon each. Pt is a 5d surrogate for the Pu 5f electronic structure. Here, a strong Fano effect is observed in the 5d states, regardless of whether the sample has long or short-range order. This result can be seen in Fig. 3. The absence of the necessity of long-range order means that single crystal samples are not required for this experiment in Pu.

Thus, we propose that the most efficacious way to proceed with Pu, particularly to investigate the nature of electron correlation in the Pu 5f states [1,19], is via Fano Spectroscopy.

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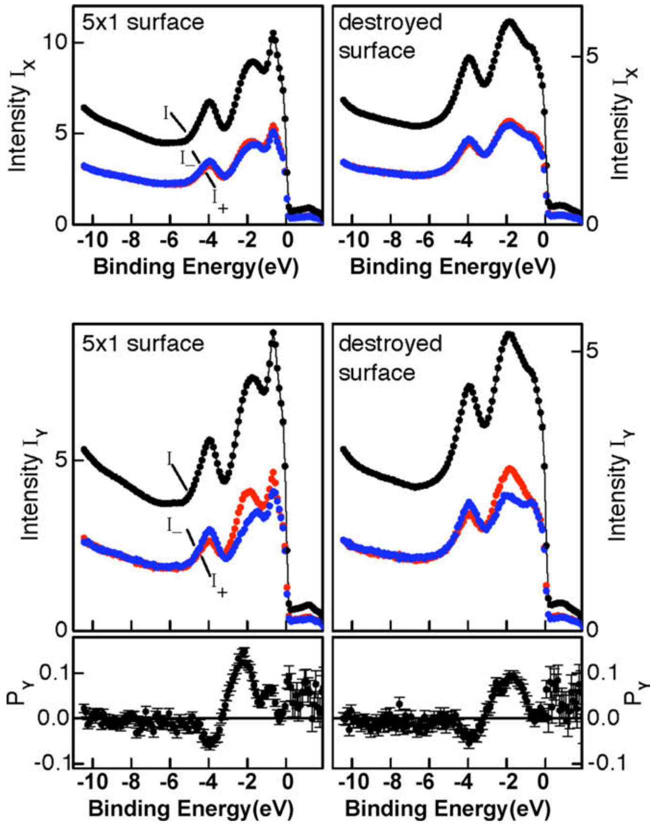

Fig. 3. Shown here are the Fano Spectroscopy results for Pt [15]. Spin resolved photoemission spectra obtained with unpolarized He I(hv = 21.2 eV) light for normal emission from the valence bands of Pt(001). Upper panel for *Px* component: The spin integrated total intensity I(black) and spin separated partial intensities I+ in red and IÀ in blue are shown for 5 × 1 surface and destroyed surface. Since the measured spin polarization *Px* is zero, the partial intensities I+ and IÀ are identical. Lower panel for *Py* component: The spin integrated total intensity I(black) and spin separated partial intensities I+ in red and IÀ in blue are shown for 5 × 1 surface and destroyed surface. The measured spin polarizations *Py* for 5 × 1 surface and destroyed surface are shown. Note the loss of the 5 × 1 reconstructed surface state intensity at the binding energy of 0.66 eV with the destruction of the surface order for both *x* and *y* components.

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