Electronic Structure of α- and δ-Plutonium

Theory vs experiment

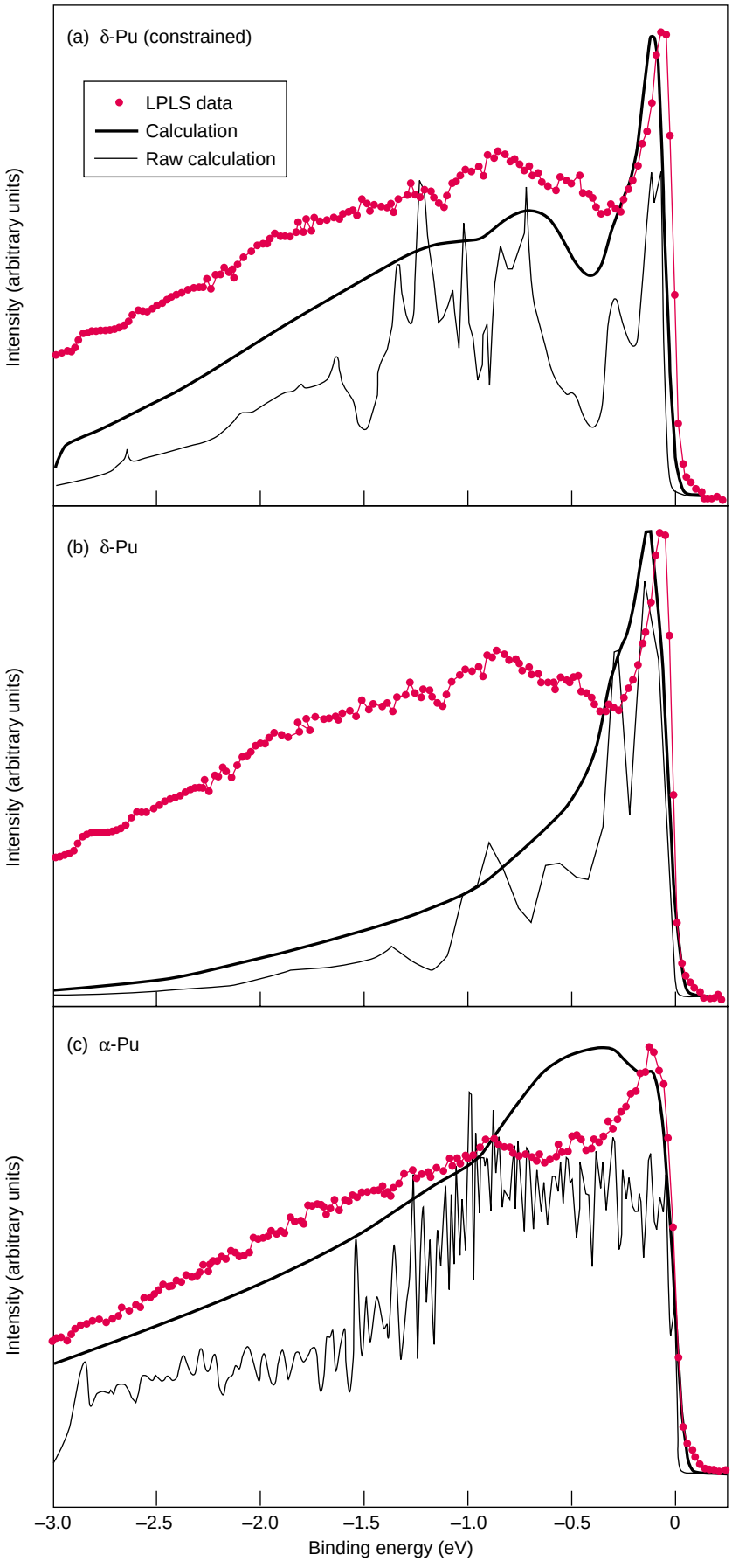
Aloysius J. Arko, John J. Joyce, and John M. Wills

Photoelectron spectroscopy (PES) provides a direct means for comparing the calculated density of states with the measured electronic structure. Because the photoemission cross sections vary strongly with both photon energy and orbital symmetry, one must choose for comparison spectra at a photon energy at which the d and f cross sections are about equal. That value turns out to be near hν = 40 electron-volts (eV), which is conveniently near the helium II resonance line. For this reason, we compare the calculated results with the data from a spectrum obtained with helium II radiation at a temperature of 80 kelvins and with a resolution of about 75 milli-electron-volts (meV). (See the article "Photoelectron Spectroscopy of α- and δ-Plutonium" on page 168.)

Figures 1(a)–1(c) show this comparison for α- and δ-plutonium. In each frame, the experimental curves are the red data points, the unbroadened calculated density of states is shown by the thin black lines, and the broadened calculated density of states is represented by the thick black lines. Broadening of the calculated spectra is necessary for comparison with experiment. A photoemission spectrum is broadened by Gaussian instrument resolution cut by the Fermi energy, and more important, by Lorentzian lifetime broadening created by the hole produced in the photoemission process, typically called a photohole. Lifetime broadening occurs because, the farther below the Fermi energy a photohole is created, the faster it is refilled from higher-lying states. Thus, this broadening is energy dependent. The density of states in Figure 1 has thus been convoluted with a Lorentzian whose full width at half maximum (FWHM) increases as $[E_0 + E_1 (E_B^2)]$, where E_B is the energy below the Fermi energy, E_0 is set to 20 meV, and E_1 is 1.1 eV^{-1} to simulate lifetime broadening of the photohole. The maximum allowed broadening is restricted to 1 eV. All calculations are broadened identically. The secondary electrons have been subtracted from the experimental data by a Shirley-type background subtraction. The constants E_0 and E_1 were chosen to fit the data in Figure 1(a). The same constants were used in all three frames.

In Figure 1(a), we compare the δ-plutonium spectrum with results of a generalized-gradient approximation (GGA) calculation in which four of the five 5f electrons are constrained to localization. Globally, the experimental δ-plutonium spectrum is well reproduced by the calculated spectrum, suggesting that perhaps this is a good starting point for a basic understanding of plutonium. This notion is reinforced by the observation that the band calculations predict some admixture of 5f and 6d character for the narrow peak, the amount depending on the choice of constraint conditions as needed for interpreting the photon energy dependence. However, at present, the calculation would place the narrow feature 60 meV below E_F as opposed to exactly at E_F, where it is found experimentally. The exact nature of this discrepancy is not understood at this time.

Figure 1(b) compares the δ-plutonium spectrum with results of an unconstrained GGA calculation in which all 5f electrons are allowed to be itinerant. In this calculation, the bulk of the 5f density



of states is found to be contained in a narrow region within 0.5 eV of the Fermi energy (similar to uranium results). This result is clearly at odds with experiment and reinforces the notion that at least some of the 5f electrons are localized.

The α-plutonium calculation and measured spectrum are compared in Figure 1(c). Some puzzling problems become evident because the sharp structure near E_F, clearly observed experimentally, is not well reproduced in an unconstrained GGA calculation. Conventional wisdom states that α-plutonium is much like a transition metal with conventional bands. A sharp peak at the Fermi energy would suggest that even this transition-like material exhibits strong correlation effects. But the sharp feature in the α-plutonium spectrum occurs at 100 meV below E_F, and it therefore calls into question the correlation effects. Moreover, one would not anticipate electron-electron correlations in a system with a temperature-independent susceptibility as well as a densely packed crystal structure, in which direct f-f overlap is possible. Nonetheless, we must recall that α-plutonium 4f core levels show satellite behavior similar to, yet not as intense as, that in δ-plutonium. Perhaps correlation phenomena are important in spite of the 5f maximum occurring at 100 meV below E_F. A reasonable calculational approach for α-plutonium might be one of renormalized bands, in which the Hubbard Hamiltonian is introduced as a perturbation on GGA-derived bands. Variation of the Coulomb correlation energy interaction U controls the strength of the electron-electron correlations. This approach may solve the problem for α-plutonium but is more problematic for δ-plutonium, whose GGA-calculated bands are too narrow compared with experiment. The structure at 1 eV may not be reproduced by renormalization. ■