

X-ray photoemission study of δ -Pu stabilized by 1 wt. % Ga: Electronic structure and sputter-induced surface phase transformation

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Photoemission spectra of the core ($4f$) and valence levels of Ar-ion-sputtered, Ga-stabilized δ -Pu are similar to those of α -Pu. This disordered α - or β -like surface layer is readily transformed by mild annealing (225 °C) to the δ allotrope as evidenced by profound changes in $4f$ spectrum. We attribute these changes to a transition from predominantly f -like final-state screening in the α -like phase to predominantly d -like screening in the fcc allotrope. The latter also shows a broadened valence band, presumably resulting from many-body effects associated with incipient localization of the $5f$ electrons.

On a qualitative level many of the unusual physical properties of the light actinide elements are understood to result from the influence of the $5f$ electrons. The anisotropy of the f angular wave functions, for example, induces low-symmetry crystal structures in the room-temperature phases of U, Np, and Pu. This effect is evidenced most dramatically in the monoclinic α and β phases of Pu with unit cells containing 16 and 34 atoms, respectively. In addition to these complicated low-temperature allotropes, Pu passes through four other phases below the melting point and unquestionably qualifies as the culmination of actinide complexity. The best known of the higher temperature phases is δ -Pu which can be stabilized to room temperature by the addition of a few wt. % of Al or Ga. Although its fcc crystal structure suggests more typical metallic behavior, the δ phase is anomalous in that its volume (20% greater than α) is larger than would be expected for a normal bandlike metal, but smaller than for a rare-earth-like electronic configuration with localized $5f$ electrons. Other probes of electronic structure are suggestive of a tendency toward $5f$ localization, which we know occurs at Am (Refs. 1 and 2), but do not provide unambiguous insight into the details of changes in orbital participation in the bonding. The peculiar electrical resistivity behavior of α -Pu (Ref. 3), for example, was interpreted in terms of spin fluctuations, an indication of a narrow f band; however, magnetic ordering does not occur in either the α or δ phases.

The large lattice constant and very large electronic specific heat⁴ (53 mJ/g atom K²) of δ -Pu suggest a narrow $5f$ band such as those thought to exist in the heavy-fermion systems of U.^{5,6} In the U systems the U-U separations are too large for direct f - f overlap and the narrow band arises from $5f$ hybridization with ligand orbitals. That calculated bandwidths are not consistent with the large electronic specific heat in these materials⁶ implicates many-body effects as important contributing factors. The relevance to the present work is that enhanced low-temperature heat capacity is accompanied by significant broadening of both the filled (photoemission) and unfilled (bremsstrahlung isochromat spectroscopy) parts of the valence band relative to the predictions of local-density calculations.⁷⁻⁹ We hasten to add, however, that the

narrow-band formation and apparent trend toward localization in U is observed only in the presence of alloying elements which mediate the subtleties of $5f$ hybridization near the edge of the itinerant range. In Pu a nearly equivalent spectrum of behavior is seen in the allotropes of a single element.

The core-level chemical shifts and satellite structure commonly seen in lanthanide and actinide photoemission spectra are equally informative with regard to diagnosing $5f$ bonding and hybridization. Because of their compact radial functions, the $5f$ electrons exhibit greater Coulombic interaction with the core levels than do the $6d$ or $7s$ orbitals. Consequently, changes in $5f$ occupation are rather sensitively reflected in core-level (e.g., $4f$) binding-energy shifts. In U intermetallics these shifts amount to no more than a few tenths of an eV except in a few systems where the $5f$ occupation has been reduced to about 2 as confirmed by magnetic behavior. UPd₃ appears to fall into this category. It is therefore of interest to see whether the substantial volume and symmetry changes between α and δ -Pu cause a similar change in $5f$ occupation and hence $4f$ binding energy.

Complicating the interpretation of core-level shifts are final-state effects arising from the response of the system to the creation of a core hole. Of particular importance is the attempt of the core-ionized atom to rearrange its valence configuration to screen the excess positive charge. In f -electron systems this is most efficiently accomplished by filling a vacant f level which, by virtue of its interaction with the core hole, has been pulled down in energy below the Fermi level, E_f . The probability of attaining this "well-screened" final state depends on the mixing or hybridization between the energetically lowered f state and the source of screening charge—the conduction band. The absence of $4f$ satellites in α -U, for example, indicates strong $5f$ conduction-band mixing, enabling the system to assume an f -screened final state. Am, on the other hand, exhibits a $4f$ spectrum with only a weak feature attributable to f screening, the main peak representing a $6d$ -screened final state.² This is consistent with the low spectral weight at E_f and multiplet structure in the valence-band spectrum both of which signal complete localization of the $5f$ levels. It is reasonable to assume, therefore, that

Pu will show intermediate behavior and that some qualitative indication of changes in $5f$ itineracy and hybridization between the phases will be evident in the spectra.

The alloy employed in this study was high-purity electrorefined metal which was stabilized in the δ phase by the addition of 1 wt. % Ga. Ga was never detected in the x-ray photoemission spectroscopy (XPS) spectra of this material and is therefore of no concern as a spectral interference. Sample cleaning was effected by repeated cycles of Ar-ion etching (5 keV, 15 μ A) and annealing at 350°C. A surface free of detectable impurities except oxygen was obtained in this way. The concentration of the latter corresponded to about $\frac{1}{6}$ (atomic) of that of Pu. After 2 h in the spectrometer at 1.3×10^{-8} Pa (1×10^{-10} Torr) the oxygen signal increased to about twice its initial value, but no changes in either the core or valence spectra were observed. We believe, therefore, that the spectra are free of oxygen-induced artifacts.

The $4f$ spectra of an Ar-ion-etched surface before and after annealing are shown in Fig. 1. The spectrum of the unannealed surface is quite reminiscent of α -Pu except that the broad shoulder, about 2.5 eV to higher binding energy, is considerably more intense. The sharp maximum of the $4f_{7/2}$ peak is at a binding energy of 422.2 eV, nearly the same as that reported for α -Pu.^{10,11} Annealing at 225°C produces the dramatically different spectrum also shown in Fig. 1. The broad satellite feature is now dominant and only a trace of the sharp low-binding-energy peak remains. The new peak maximum is at a binding energy of 424.8 eV, only slightly lower than that reported for Pu₂O₃.¹¹ That the new feature was not due to oxide formation was established by examination of the O 1s line which increased only slightly in intensity. The asymmetry toward higher binding energy also would not be expected for an oxide, since it normally results from electron-hole production near the Fermi level in metals. Our suspicion that the annealed surface was in fact δ -Pu

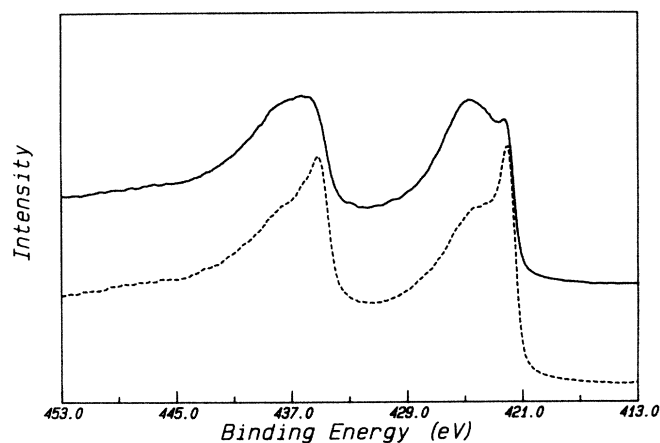


FIG. 1. Photoemission spectra of the $4f$ levels of a 1 wt. % Ga δ -stabilized Pu sample. The lower spectrum was obtained on a specimen which had been Ar-ion etched at 5 keV; the upper spectrum resulted when the sample was annealed briefly at 225°C.

was confirmed by obtaining a spectrum at 350°C where the δ phase is stable. The low-binding-energy feature was less distinct at the higher temperature, but the peak position and shape were otherwise unchanged.

Preferential sputter removal of one component of binary alloys is a well-known phenomenon in surface analysis and it is this which we believe is responsible for the surface transformation to an α -like phase. Unfortunately, we were unable to detect Ga in the alloy even after annealing, but it does not seem unreasonable that the much lighter Ga atoms would be selectively depleted in the surface region, allowing the alloy to revert to the room-temperature-stable α phase. We also found that reducing the ion-beam energy led to an increase of the intensity of the broad high-binding-energy feature suggesting that the thickness of the altered surface layer had been reduced, so that a greater contribution to the spectrum arose from the pure δ -Pu beneath it. Ga is apparently quite mobile in this disordered region and only mild annealing (100° below the bulk transition temperature) is required to effect the transformation back to the δ phase. We are only able to characterize the surface phase via its XPS spectrum which closely resembles published spectra of α -Pu. It seems likely, however, that other phases are present simply because it is difficult to imagine an abrupt interface between allotropic phases with a volume difference of nearly 20% and with radically different crystal structures (monoclinic and fcc).

Although the sharp low-binding-energy feature and broad satellite undoubtedly represent differently screened final states, their exact nature is less clear. Naegele, Mannes, Spirlet, and Müller² described the satellite in α -Pu and the main peak in Am as poorly or $6d$ -screened final states in analogy with the light lanthanides.¹²⁻¹⁴ More recent studies of Th (Refs. 15 and 16) and U (Ref. 17) intermetallics have shown, however, that the complexity of the screening processes in the actinides makes such descriptions inadequate. These difficulties arise because the greater radial extent of the $5f$ wave function leads to decreased Coulomb correlation energies (U_{ff}) and hence decreased energy separation of states of differing f occupation number in both the ground and core-ionized states. For example, assigning the $4f$ spectral features of UCu₅ (Ref. 17) to f^4 , f^3 , and f^2 final states leads to an unrealistically small U_{ff} value of 0.6 eV. The authors interpreted this to mean that the U final states were not pure $5f^n$ configurations, but rather mixtures of such states.

An additional problem is the use of terminology appropriate for the Anderson impurity model in describing actinide systems. A basic component of this theory is f -conduction-band hybridization, where the f level is understood to indicate a localized state, and the conduction band to consist of itinerant $5d$ and $6s$ states. In the light actinides the conduction band contains appreciable f character and empty itinerant f states are certainly available for core-hole screening. Such screening is not the same as the localized atomiclike states arising from occupation of states which have been pulled down in energy by 5–6 eV by the core-hole potential. The term “ f screening” is thus somewhat ambiguous as is the use of f occupation numbers in describing final-state configurations. In

the absence of detailed theoretical results the terms "well screened" and "poorly screened," which make no assumptions about the orbitals involved in screening, may be preferable. It is important to recognize, however, that poorly screened final states with f character are possible and indeed seem to be the best explanation of the $4f$ XPS and $3d$ XAS of α -Pu.

In order to clarify the relationship between the photoemission screening channels and electronic structure we now focus on the significant differences in band structure which exist between α and δ -Pu. No band theory results for the complicated α -Pu structure are available, but the high-resolution UPS results of Naegele¹⁸ together with the δ -Pu band results of Weinberger, Boring, and Smith¹⁹ permit some comparison of the densities of states (DOS). The occupied $5f$ band in δ -Pu consists of a narrow feature about 0.4 eV wide centered about 0.3 eV below E_f . The d -like DOS is broader, extending to about 1.5 eV below E_f , but represents a much smaller contribution to the total DOS. Both the f - f overlap and f - d hybridization show exponential dependences on site separation (r^6 and r^7 , respectively) and, together with the reduction in symmetry, produce a large increase in bandwidth in α -Pu. The UPS valence-band spectrum¹⁸ shows a width [full width at half maximum (FWHM)] of slightly over 2 eV and a long tail out to about 5 eV. Unfortunately, the extent to which lifetime broadening and many-body effects affect to spectral width is uncertain, but it is reasonable to estimate the overall α -Pu bandwidth at 2–3 times that of δ .

Because, as evidenced by the very narrow f band, the f bonding in δ -Pu is considerably more tenuous than in α , the effects of core-hole creation are expected to be quite different. In the former case the $5f$ electrons are believed to be on the ragged edge of localization and the creation of a core hole is sufficient to disrupt the local $5f$ bands and withdraw the $5f$ states from E_f . This rare-earth-like final state would have only the $6d$ and $7s$ conduction states remaining at the Fermi energy available for screening. The broad high-binding-energy peak in the δ (annealed) spectrum is believed to represent such a final state. The weak sharp feature may be a remnant of the locally f -screened final state and/or an f^6 contribution to the ground state which band calculations show to exhibit a $5f$ occupation of 5.15.²⁰

For the reasons discussed above the $5f$ bonding in α -Pu is considerably more robust and undoubtedly persists in the core-ionized final state. The nature of the poorly screened final state is largely determined by the l -projected DOS at E_f and is expected contain both f and d character. That quasilocalized or excitonic f states are involved in the screening process is supported by (actually, suggested by) the $3d$ XAS results of Bonnelle, Courtois, and Calais.²¹ Because the x-ray absorption process obeys dipole selection rules, only f states are probed, and in this respect the spectra are a useful complement to XPS data. The spectrum of α -Pu shows two peaks of roughly equal intensity with nearly the same energy separation as the features in the $4f$ photoemission spectrum. The lower-energy absorption, which occurs at the same energy as the single peak in the δ -Pu spectrum, must represent a transition to a localized $5f$ level, i.e., $3d^{10}5f^5 \rightarrow 3d^9 5f^6$. The

only reasonable assignment for the higher-energy transition, which must also be to an f -like state, is one terminating in an extended state at E_f . The XPS and XAS final states then differ only in the core level containing the hole, but the Coulombic stabilization of the valence electrons should not be significantly different in the two cases. A similar opinion was expressed by Baer.²²

The apparent ease with which the $5f$ levels can be uncoupled from the conduction band is fascinating and has important implications for the interpretation of core-level binding energies. Indeed, the very limited XPS data available for Pu compounds seems to indicate that Pu $5f$ -ligand hybridization is much less effective than in the lighter actinides. The study of PuSb by Baptist *et al.*²³ found the Pu $4f_{7/2}$ peak at a binding energy 4 eV higher than the metal, whereas in USb only a very small chemical shift is observed. The large $4f$ chemical shift in PuSb together with the recession of $5f$ spectral weight from E_f , show clearly that $5f$ localization has occurred in this material and forced the system to adopt a $6d$ -screened final state. Note that the binding energy is nearly as high as in PuO₂, although in the latter case the chemical shift is consistent with those of UO₂ and NpO₂ (Ref. 24) and seems to be primarily a consequence of charge transfer in the initial state. Ghijzen²⁵ studied PuFe₂ after sputtering and scraping and concluded that Pu oxycarbide and/or carbide were present. The $4f$ spectrum he obtained closely resembles that of δ -Pu however, and we believe that the feature assigned to an oxide/carbide is in fact a poorly screened final state. That an f -screened state also exists in this compound can be attributed to the Pu $5f$ -Fe $3d$ hybridization being stronger than in compounds of the heavier chalcogenides or pnictides. Strong f -ligand hybridization is known to exist in Ce intermetallics of Fe and Co and their congeners, and we expect to find a similar situation for Pu. Present (admittedly scanty) evidence suggests that the Pu $4f$ spectral features may be a more sensitive probe of $5f$ bonding involvement than valence-band spectra.

Shown in Fig. 2 are valence-band spectra obtained un-

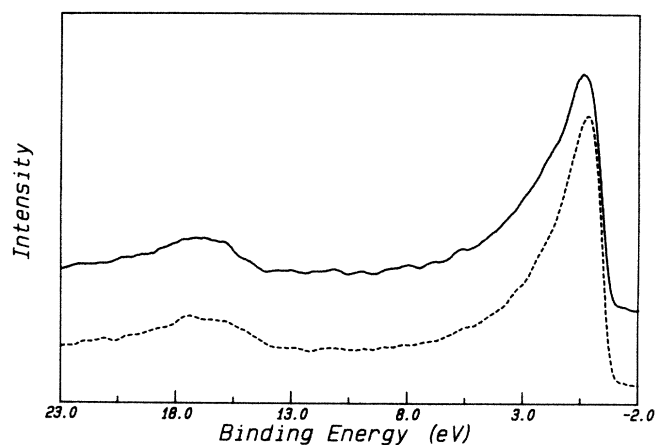


FIG. 2. Valence-band photoemission spectra obtained under the same conditions as Fig. 1. Note the increased bandwidth of the δ -Pu (upper) spectrum and the weak structure on the high-binding-energy side of the peak.

der the same conditions as the $4f$ spectra. The α -like sputtered surface shows a rather broad and featureless $5f$ band similar to what we²⁶ and others¹⁸ found previously. Also shown is the annealed δ -Pu spectrum which is about 15% broader (FWHM) than α , as opposed to the large decrease (50–70%, see above) one would have expected in a well-behaved bandlike material. We also found some suggestions of structure on the high binding-energy side of the band, although it was always weak and seemed to depend somewhat on the annealing conditions. The $5f$ bonding and f - d hybridization are undoubtedly less important in δ than in the α allotrope, so that appearance of band structure at higher binding energies in the former is unlikely. This expectation is supported by the calculation of Weinberger *et al.*¹⁹ which shows a very low density of states in this region. A more probable source of the extra intensity is a localized f hole final state, as has been discussed for U by Johansson *et al.*²⁷ In this case the photo-

emission process leaves a localized, atomiclike final state which should exhibit multiplet structure. Unfortunately, the structure we observe is too weak to be identified with the multiplet calculations of Gerken and Schmidt-May for the $5f^5 \rightarrow 5f^4$ process.²⁸ If this assignment is correct, the localized states should be separable from the rest of the band via their enhanced intensities in resonant photoemission.

To summarize, the nearly localized $5f$ electrons of Pu are readily decoupled from the conduction band by the changes in atomic volume and symmetry accompanying the α to δ phase change. The decreased hybridization causes dramatic changes in the final-state screening mechanism. Also observed is a broadening of the $5f$ -dominated valence band suggestive of a contribution from (unresolved) multiplet structure arising from a localized-hole final state.

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