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Pu 4f XPS Spectra Analyzed in the Anderson Impurity Model

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X-ray photoemission spectra of the α,β,γ, and δ phases of Pu have been analyzed using the Gunnarsson-Schonhammer implementation of the Anderson impurity model. Changes in the relative intensities of the two spectral features representing mixed f^5 and f^6 final states are in reasonable agreement with the model's predictions. The coulomb terms, U_{ff} and U_{fc}, are quite consistent with those derived from atomic and LDA calculations. Multiplet structure, which agrees with atomic calculations for $4f^{13}5f^5$, strongly suggests 5f localization in the final state.

Keywords: Pu, 4f, XPS , Anderson Model

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I. Introduction

It has long been recognized that because of 5f-electron localization the actinide elements beyond Pu exhibit rare-earth-like behavior, whereas those with Z< 95 constitute a transition-metal-like sub-series. A large volume increase and the appearance of local-moment magnetism (at Cm and beyond) and "normal" crystal structures are among the properties which signal the change in electronic structure.

Pu finds itself in the unique position of having available an atomic correlation energy which is very close to that gained by 5f-band formation. It is this competition between band formation and localization which is believed to be responsible for the striking variety of crystal structures and atomic volumes of plutonium's six allotropes. Although its magnetic susceptibility and resistivity are suggestive of f localization, Pu does not reach this limit as a pure metal [1].

The existence of 6 allotropes in Pu presents a unique opportunity for understanding the effects of structural and volume changes on electronic structure as probed by photoemission and other techniques. In the absence of many-body effects, the increase in symmetry and volume in the higher

temperature allotropes would be expected to cause band narrowing and should be manifested in valence-band spectra. That this does not occur is one clear indication that one-electron theory does not accurately capture the physics of 5f electron behavior in this element. Recent high-resolution UPS and resonant photoemission of δ-Pu do indicate an overall recession of spectral weight from E_f, consistent with f localization, as well as the appearance of a sharp feature with a binding energy of 23 meV [2]. The width of the f manifold, however, is larger than in the α phase despite the large (20%)increase in atomic volume. Recent fully relativistic LDA calculations [3] also predict an f bandwidth much smaller than is observed in photoemission.

Photoemission data for the 4f levels of the α and δ phases have been reported previously[4], and the present study was undertaken so that the evolution of the characteristic spectral features could be more clearly identified for the first four phases. We also report the results of applying the Anderson impurity model to the spectra of these phases.

II. Experimental

Measurements were performed on a coupon of high-purity, electrorefined Pu. Spectra of the various phases were obtained at the temperature at which each is normally stable. The surfaces remained essentially oxygen-free for at least an hour after sputter-cleaning.

III. Results and Discussion

Background-subtracted spectra of the α and δ phases of Pu are shown in Figs. 1 and 2. In both cases one observes a sharp feature at about 422 eV

and a much broader shoulder about 2.5 eV to higher binding energy. The relative intensity of the latter feature is seen to increase dramatically in the δ phase suggesting that final-state effects involving 5f screening are responsible. Weak but reproducible structure is also evident on the broad peak.

The above-mentioned phenomena have previously been ascribed to well-screened ($5f^6$) and poorly-screened ($5f^5$) final states. The simplest model available for describing the system more quantitatively utilizes the Anderson impurity Hamiltonian. The success of this approach is well documented for Ce [5], and, even though some additional approximations are implicit in applying it to an f^5 system, it does not seem unreasonable to believe that there are valid parallels in the electronic processes involved.

In order to compare theoretically-predicted spectral weights with experiment one must make some assumptions about peak shapes. Because there is significant overlap of the two spectral features and neither is well described by the usual peak-shape functions (e.g. Doniach-Sunjic) is was necessary to employ an empirical fitting procedure to determine relative areas. Using a Lorentzian for the sharp peak and an asymmetrical double sigmoidal for the broad peak (PeakFit, Jandel Scientific) gave a sensible deconvolution. A number of other functions were tried and gave very similar results. The theoretical calculation yields a spectral-weight distribution in histogram form. With the parameter set appropriate for Pu (see below) the calculated distribution contained two sets of states which we associate with the observed peaks. To compare with experiment we generated a spectrum using the least-

squares fitting parameters and placing these peaks, weighted by the calculated spectral weights, at the two centers of gravity from theory. Figs.1-2 show the results of this procedure.

In selecting the coulomb and hybridization parameters for Pu one is guided by the knowledge that the greater spatial extent of the 5f radial wave function will dictate smaller values of U_{ff} and U_{fc}, but larger hybridization than obtain for Ce. Estimates of U_{ff} for Pu range from 3.3 to 4.4 eV [] and thus are roughly half as large as for Ce. Similarly reduced values of U_{fc} were found to give good agreement with experiment. Values of ε_f , the bare f energy, were set such that the experimental absence of an identifiable f^4 peak was reproduced.

The striking difference in the width and shape of the f^5 and f^6 peaks sets the Pu spectrum apart from any of the rare earths or lighter actinides. The presence of non-spurious structure, particularly in the δ-phase spectrum, points to a rather unique broadening mechanism. Because core-ionized Pu should be electronically similar to Am, a localized f^6 system, we felt multiplet structure might be responsible for these phenomena. To test this hypothesis we calculated atomic photoionization cross-sections for the $4f^{14}5f^5 \rightarrow 4f^{13}\ 5f^5$ process. Neither the f^5 ground state ($^6H_{5/2}$) nor any other low-lying state produced structure even close to experiment. Only by assuming all states (about 2500) of the configuration are present could reasonable agreement be obtained.

That the f^5 feature is broader than in Pu_2O_3, in which a magnetic ground state exists, suggests that a (screened) magnetic ground state, by itself, is not an adequate representation of the metal.

References

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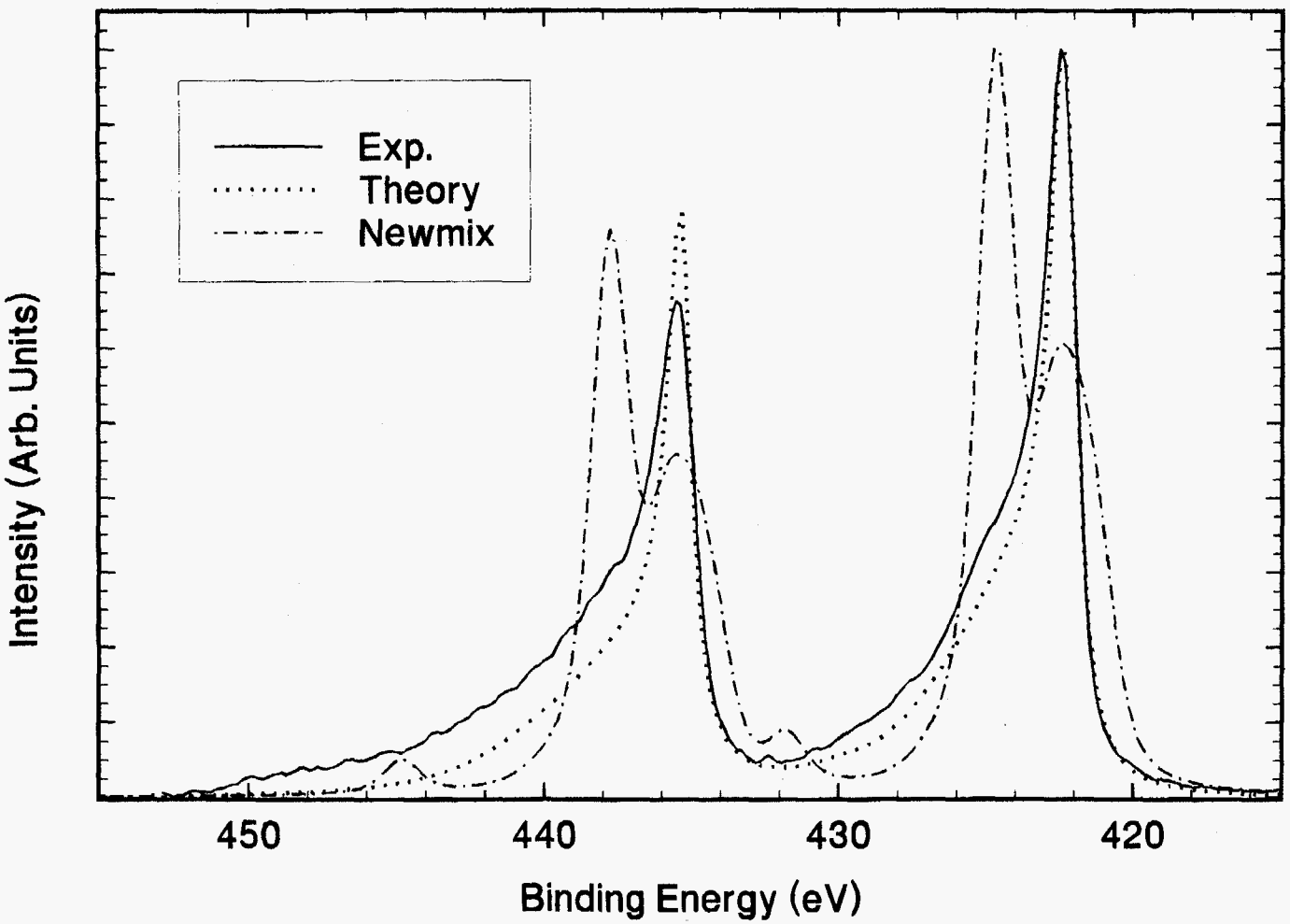
[5] See for example, Narrow-Band Phenomena-Influence of Electrons with Both Band and Localized Character, eds. J. C. Fuggle, G. A. Sawatzky, and J. W. Allen, (Plenum, New York, 1988).

Figure Captions

Fig. 1 Comparison of the experimental 4f spectrum of α-Pu with the broadened calculated state density (NEWMIX) and a simulated spectrum using calculated intensities and experimental peak shapes (see text).

Fig. 2. Comparison of the experimental 4f spectrum of δ-Pu with the broadened calculated state density (NEWMIX) and a simulated spectrum using calculated intensities and experimental peak shapes (see text).

II.


ALPHA Pu
-1.5/6/4.4/0.285
Exp.
Theory
Newmix
Intensity (Arb. Units)
450
440
430
420
Binding Energy (eV)

DELTA Pu

-2.38/6.0/4.4/0.169