PHYSICAL REVIEW B VOLUME 23, NUMBER 2 15 JANUARY 1981

Satellite structure in the 5*p* and 5*s* x-ray-photoelectron spectra of the actinides

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(Received 25 July 1980)

In this article, we report the results of a configuration-interaction study of the 5*s* and 5*p* hole (denoted by $5\underline{s}$, $5\underline{p}$) states in Ra, Th, and U atoms. Our most important finding is that all of the major satellite features in the $5\underline{p}$ spectra of these solids can be accounted for by an atomic model without recourse to "shakeup" losses arising from extra-atomic relaxation in the solid. Our results for the 5*s* region of the actinides show a strong $5\underline{s} \rightarrow 5\underline{p}\,5\underline{d}\,5f$ interaction and suggest that this level should also be significantly perturbed by the continuum channels $5\underline{p}\,5\underline{d}\epsilon f$.

An early indication of the importance of many-electron effects in photoemission was the observation of a splitting of the $5p_{3/2}$ level in the x-ray photoelectron (XPS) spectrum of the Th, U, and Pu metals and compounds by Novakov and Hollander.[1] Bancroft, Sham, and Larsson[2] suggested that this structure, as well as that observed in other actinide compounds, could be attributed to a configuration interaction (CI) between the 5*p* hole and a $5d^2 \rightarrow 5p5f$ excitation. This interpretation was also forwarded by Kowalcyzk,[3] who pointed out the analogy with the $4d^2 \rightarrow 4pmf$ (m discrete or continuous) mechanism known to be important in the lanthanide series.[4-7] These interactions lead to large satellites in the XPS spectrum because the oscillator strength associated with the "allowed" (one-electron) transition from the 5*p* orbital ($5p^6 5d^{10} 5f^n \rightarrow 5p^5 5d^{10} 5f^n$) is shared with "forbidden" final states arising from $5p^6 5d^8 5f^{n+1}$. In CI terms, the mixing between $5\underline{p}$ and $5\underline{d}^2 5f$ (the underline denotes a hole) is strong because it describes an internal (intrashell) correlation.[8] Not only are the two-electron integrals coupling the configurations large because of an appreciable radial overlap between functions of the same principal quantum number, but, since the orbital energy sum $\epsilon(5p) + \epsilon(5f) \simeq 2\epsilon(5d)$, the two configurations are nearly degenerate. For similar reasons, an appreciable interaction between $5\underline{s}$ and $5\underline{p}5\underline{d}5f$ is also expected. Wendin and co-workers[5] discuss this in terms of dynamic correlation between dipolar density fluctuations of a $5\underline{p}$ hole ($5\underline{p} \rightarrow 5\underline{d}$) and 5*d* electrons ($5d \rightarrow 5f$).

Solid-state effects are also expected to contribute to the satellite structure.[9] Sham and Wendin[10] have recently proposed that much of the extra-atomic relaxation in the metal is accomplished by the 5*f* band, which results in structure associated with "electron-hole pair excitations from occupied to empty levels within the 5*f* band." In order to assess the importance of these contributions, it seemed worthwhile to compare the quantitative predictions of an atomic CI model with the spectra of some of the actinide metals and compounds.

The $5\underline{s}$ and $5\underline{p}$ hole states of Ra, Th, and U were investigated. The orbitals for each configuration were determined by a relativistic Hartree-Fock approach in which the mass-velocity and Darwin terms are iterated to self-consistency,[11] and the Fock operator is a configuration average. Spin-orbit and multiplet effects are included in the CI matrix. The large number of terms which arise from the open shells in these systems necessitated some approximations. The dimension of the CI matrix for the $5\underline{p}$ hole state of radium, with ground state (Rn)$7s^2$, is relatively small, since the only coupling which must be considered is between the open shells $5\underline{d}^2 5f$ and $5\underline{p}$. In Th, (Rn)$7s^2 6d^2$, one has the additional complication of the 6*d* spectator electrons, and to maintain a manageable calculation we averaged the coupling of the $5\underline{d}^2 5f$ multiplets with the $6d^2$ terms. Because the interactions between shells of different principal quantum number are relatively weak, in this case of the order of 1.0 eV, this assumption is justified for our purposes. Finally, in U, (Rn)$7s^2 6d 5f^3$, we have the interactions among the open shells $5\underline{p}5f^3 6d$ and $5\underline{d}^2 5f^4 6d$. Here the multiplet couplings involving the spectator 5*f* electrons cannot be so easily dismissed. They were initially incorporated in an average sense, in order to give us a rough idea of the CI effects in U. A later calculation, in which all the multiplets of $5\underline{p}5f$ and $5\underline{d}^2 5f^2$ were included, provided an estimate of the broadening of features expected when multiplet splitting involving the spectator *f* electrons is introduced.

The results are compared with the available experimental data in Fig. 1. The $5\underline{p}_{1/2}$ hole state is only weakly perturbed by the interaction; it shifts to slightly higher binding energy and a weak satellite with ~10% of the intensity of the primary $5\underline{p}_{1/2}$ peak appears ~40 eV to its low-binding-energy side. The CI $5\underline{p}_{3/2}$ state splits into two major components separated by ~20 eV. In Ra, the peak at higher binding energy is mostly of $5\underline{p}_{3/2}$ character. In Th the mixing is so strong that the $5\underline{p}_{3/2}$

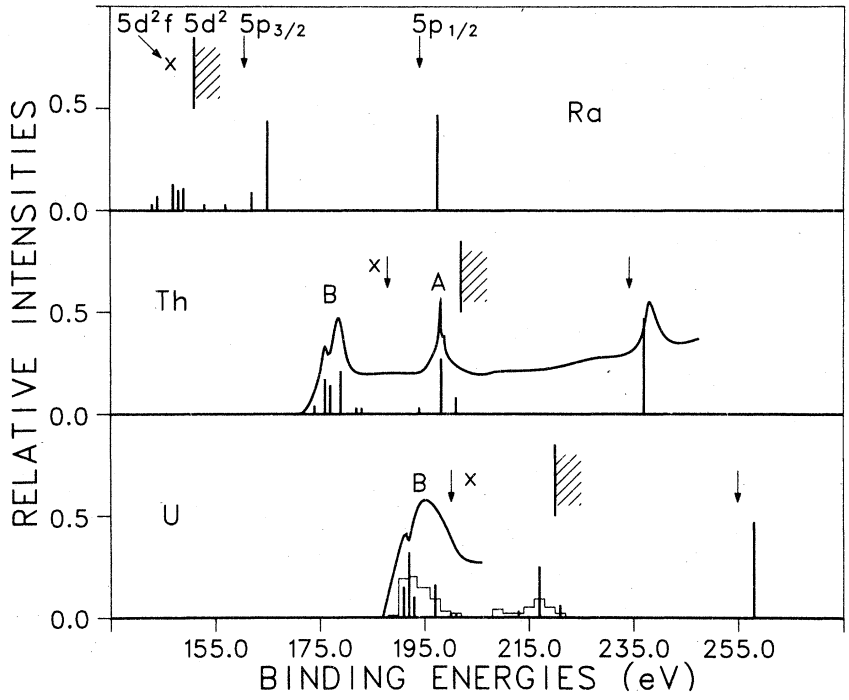

FIG. 1. CI and ΔSCF results for Ra, Th, U in the $5p$ region. Arrows, shaded areas, and ×'s represent ΔSCF results (shifted to lower binding energy by 11.0 eV) for the hole states as labeled. Theoretical relative intensities are represented by stick spectra. The experimental spectrum for Th is from Ref. 10 and for U (UO_2) is from Ref. 12. The histogram refers to the calculation in which $5p5f$ and $5d^25f^2$ multiplets were included.

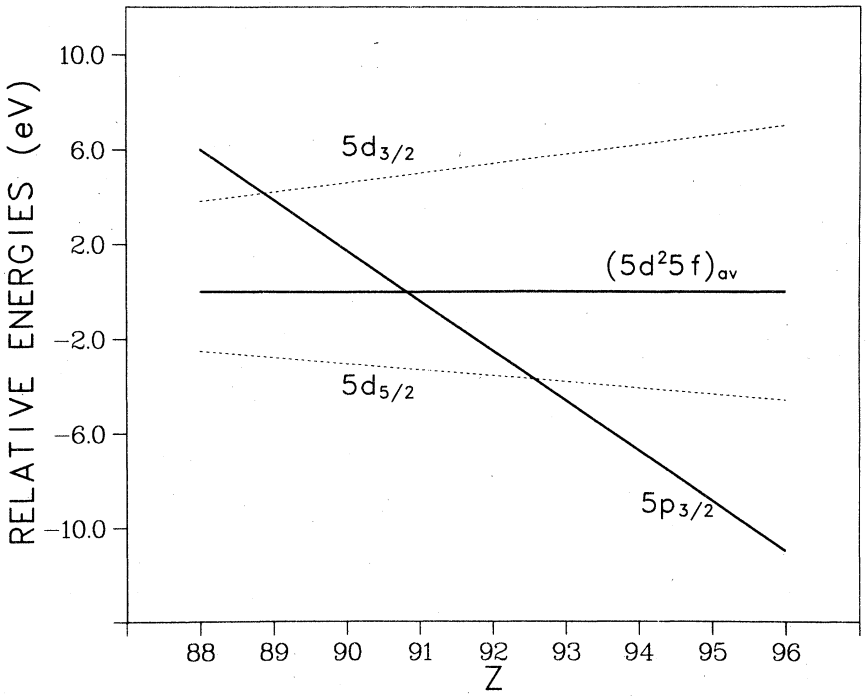

FIG. 2. ΔSCF results for the atoms Ra to Cm. The reference state is $(5\underline{d}^25f)_{av}$ and broken lines (---) represent the spin-orbit splitting of the $5\underline{d}$ orbital.

configuration is not the dominant component of any of the eigenfunctions, but by U, the low-binding-energy group emerges as predominantly $5\underline{p}_{3/2}$. This interesting transition from "shakedown" character in Ra to "shakeup" character in U (and later actinides) is due to the relative stabilities of the interacting configurations as a function of Z (Fig. 2). The $5\underline{p}_{3/2}$ configuration lies slightly above $(5\underline{d}^2 5f)_{av}$ in Ra, is degenerate near Th, and falls below at uranium.

The theoretical predictions for the onset of the double ionization limit, $5\underline{d}^2$, are also presented in Fig. 1. Note that Ra is distinct from Th and U, in that the unperturbed $5\underline{p}_{3/2}$ hole state lies in the autoionization continuum. The two-configuration model is probably inadequate here, and should be expanded to include the more general interaction $5\underline{p}_{3/2} \rightarrow 5\underline{d}^2 mf$, where m represents both discrete and continuous channels. No experimental information is available for Ra, but we expect that the discrete structure shown in Fig. 1 will be appreciably modified by the continuum channels, much as the $4\underline{p}_{1/2}$ peak is in Xe.[4]

The metallic Th spectrum is reproduced in Fig. 1. The theoretical (bar) spectra has been adjusted by 11.0 eV (to lower binding energies) to account for extra-atomic relaxation. The agreement between theory and experiment is striking. All the major features are reproduced by the atomic model. The region near 200 eV (A) is of particular interest both because it lies near the threshold of the $5\underline{d}^2$ double ionization channel, and because the shoulder has been tentatively assigned[10] as "a shakeup continuum associated with electron-hole pairs within the narrow 5f band." The present work suggests that much of the shoulder has an atomic origin. In addition to $5\underline{p}_{3/2}(^2P)$, the major components of these two peaks are the ^2D and ^2P terms arising from $d^8(^3F)f$ and $d^8(^4G)f$. In j-j coupling, $d^8(^3F_2)f_{5/2}$, $d^8(^1G_4)f_{7/2}$, and $d^8(^3F_3)f_{7/2}$ are important in the shoulder, while $d^8(^1G_4)f_{5/2}$ and $d^8(^3F_3)f_{7/2}$ are strongly mixed in the more intense features. The group of peaks in the 175-eV region are also not well described by either coupling scheme. Roughly speaking, the more intense peak is dominated by $d^8(^1G)f(^2P)$ with important contributions from the ^4F and ^4P terms of $d^8(^3F)f$, while the ^2D and ^2P terms of $d^8(^1D)f$ figure prominently in the low-binding-energy shoulder.

The mixing in U is not so strong, and most of the theoretical intensity is in the vicinity of region B. Note that relative intensities of the main peak and the shoulder are reversed by the theory. We found that this intensity pattern is sensitive to the average energies chosen; a 3-eV increase in the relative energies of the two configurations reverses this intensity distribution. Disagreements of this magnitude could also be associated with neglected

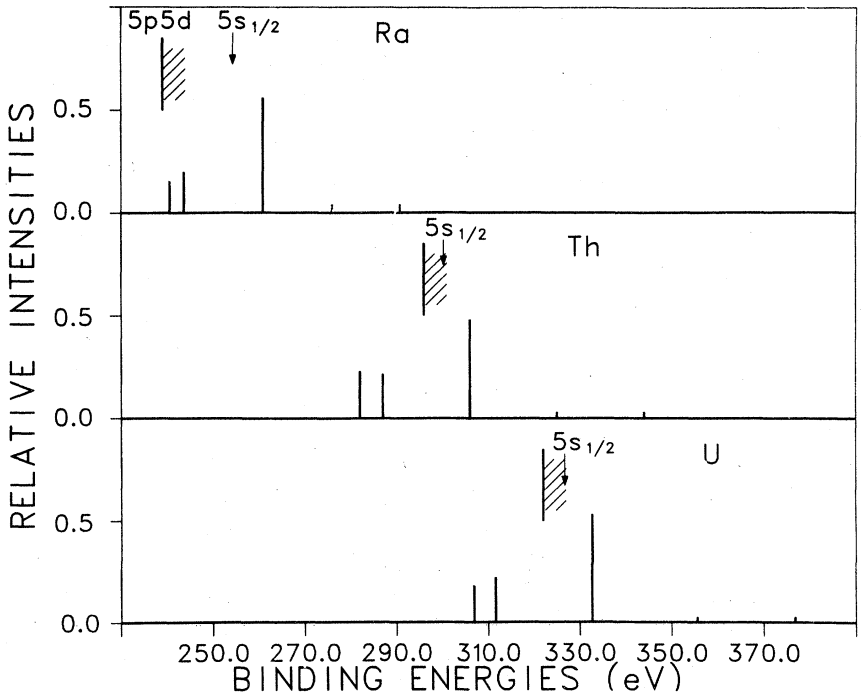

FIG. 3. CI and ΔSCF results in the $5\underline{s}$ region (labeled as in Fig. 1). Theoretical results are shifted to lower binding energy by 11.0 eV.

multiplet effects. However, their partial inclusion, via a calculation including all the multiplets of $5\underline{p}5f$ and $5\underline{d}^2 5f^2$, does not qualitatively change the theoretical band shape in this region (histogram in Fig. 1). It should also be noted that the same general profile occurs in Th(f^0), U(f^2), and Pu(f^4),[12] which would indicate that multiplet effects do not determine the basic intensity distribution in the region. In addition, Veal *et al.*[12] note that in PuO_2 and other actinide oxides the same general doublet structure is present. Multiplet coupling does, however, significantly broaden the intensity at 220 eV. These effects, coupled with the proximity of the $5\underline{d}^2$ double ionization threshold, may make it very difficult to observe distinct structure in this region. However, the fact that the experimental splitting between region *B* and the $5\underline{p}_{1/2}$ peak is much larger than theoretical ΔSCF (self-consistent field) predictions is strong evidence for substantial configuration interaction in U, even if distinct structure near 220 eV cannot be observed.

Figure 3 presents the predictions of analogous two-configuration CI calculations for the $5\underline{s}_{1/2}$ hole state. Nearly 50% of the ionization events go into multiple excitation, most of it concentrated about 20 eV to lower binding energy in states composed primarily of $(5\underline{p}_{3/2}5\underline{p}_{3/2})_{J=3}5f_{5/2,7/2}$. The model is probably inadequate here, since the unperturbed $5s_{1/2}$ level lies in the $5\underline{p}5\underline{d}$ continuum, and the results should be viewed only as indicative of a strong perturbation. A careful experimental study of this region would be interesting.[13]

In conclusion, an atomic configuration-interaction model accounts for the major features of the available data in the actinide $5\underline{p}$ XPS spectrum. Its success indicates that there are localized $5f$ orbitals near the Fermi energy in the final states of the early actinides. This, of course, says nothing about the initial-state electron distribution. The atomic model also indicates that the $5\underline{s}$ region may be significantly perturbed by the $5\underline{p}5\underline{d}$ autoionizing continuum causing a loss of spectral features in this region.

We wish to thank S. P. Kowalcyzk for helpful discussions. This work was performed under the auspices of the Department of Energy.

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[13]C. A. Colmenares (Lawrence Livermore Laboratory) has recently taken some XPS data around 300 eV in ThO_2 and told us they may have seen a feature around 290 eV at very low resolution (private communication).