Rapid Communications

Hybridization between 4f and conduction electrons and saturation of mixed valence in cerium-based systems

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(Received 15 May 1985)

The increase in $4f$–conduction-electron hybridization, as determined from deep-core photoemission studies, is compared with the increase in the mixed valence across the archetypal, continuously valence-variable system $Ce(Pd_{1-x}T_x)_3$, where $T = $ Ag or Rh. No anomaly is observed in the hybridization near $x_{Rh} = 0.2$, where the mixed valence rather abruptly saturates. Instead, a linear relationship is found between the f-d hybridization and the volume of the unit cell. This finding is consistent with a recent model which explains the valence saturation in terms of thermodynamics.

Considerable efforts have recently been devoted to the study of the anomalous properties of Ce and its compounds. Two of the anomalies related to the spectroscopic results are the two-peaked $4f$-derived structure in the valence-band photoemission,[1] and the saturation of the valence at a value of 3.2–3.3 as observed in the x-ray absorption[2,3] and x-ray photoelectron spectroscopy (XPS)[4] measurements. One important distinction between Ce and the heavier mixed-valent rare earths is the much stronger hybridization between the $4f$ and conduction states in Ce (due to the spatially more extended $4f$ orbital). The present study was motivated by the question: Is there a correlation between the unexpected valence saturation and the exceptionally strong hybridization of Ce-based systems?

In the Anderson model[5] the degree of the $4f$ instability, i.e., the mixed-valent quotient, depends on the hybridization energy Δ between the $4f$ and the conduction electrons and the energy separation between the $4f$ level and the Fermi level. The latter quantity can naively be determined from $4f$-derived photoemission experiments; however, in practice, final-state effects obscure the ground-state energetics.[1,6] On the other hand, the hybridization energy can be determined rather unambiguously from final-state effects in the deep-core x-ray photoelectron spectra, and has been evaluated for a number of Ce-based systems.[4] In the $3d$ core-hole spectra of the light rare earths, one observes, in addition to the main feature, a shakedown satellite which is well displaced to a position of smaller binding energy. The two features are differentiated in terms of their screening geometries. The main feature corresponds to a final state in which the screening of the $3d$ hole is performed by a conduction electron; whereas the shakedown satellite corresponds to screening by a $4f$ electron. The creation of the

core hole pulls an empty $4f$ level below the Fermi level. The probability that a conduction electron will fill this hole, which in turn determines the intensity of the shakedown satellite, is roughly proportional to Δ. The better screening provided by the localized $4f$ state accounts for the relatively large shift (4–5 eV) of the satellite relative to the main peak. While to first approximation the ratio of the intensity of the satellite to that of the main feature is directly proportional to Δ, this strict proportionality breaks down in more quantitative treatments of the problem.[6,7]

The system $Ce(Pd_{1-x}T_x)_3$, where $T = $ Ag or Rh, was first shown by Mihalisin, Scoboria, and Ward[8] to be a convenient "laboratory" for studying the entire range of mixed valences in Ce-based systems. Measurements of various ground-state properties[8,9] suggested that the system was trivalent for $x_{Ag} > 0.13$, and that the valence increased smoothly with decreasing Ag concentration and then with increasing Rh concentration, reaching a saturated value at $x_{Rh} = 0.2$. Subsequently, this was corroborated by L_{III} x-ray absorption-edge measurements,[3] which established the value of the saturated valence at 3.21, corresponding to a $4f$-hole count of 0.21. In order to determine the variation of $4f$–conduction-electron hybridization, Ce-derived $3d$ XPS measurements were made on numerous samples spanning the pseudobinary series $Ce(Pd_{1-x}T_x)_3$.

The samples were prepared by arc melting the constituents in an inert atmosphere followed by a five-day anneal at 800 °C. The phase purity of the fcc $AuCu_3$ structure was verified by x-ray diffraction. Compositions prepared included $x_{Rh} = 0.1$, 0.2, 0.3, 0.6, and 1.0 and $x_{Ag} = 0$ and 0.13. The samples were fractured in the photoemission measurement chamber at a pressure of $(1-2) \times 10^{-10}$ Torr; and the XPS spectra were obtained within one hour of fracturing.
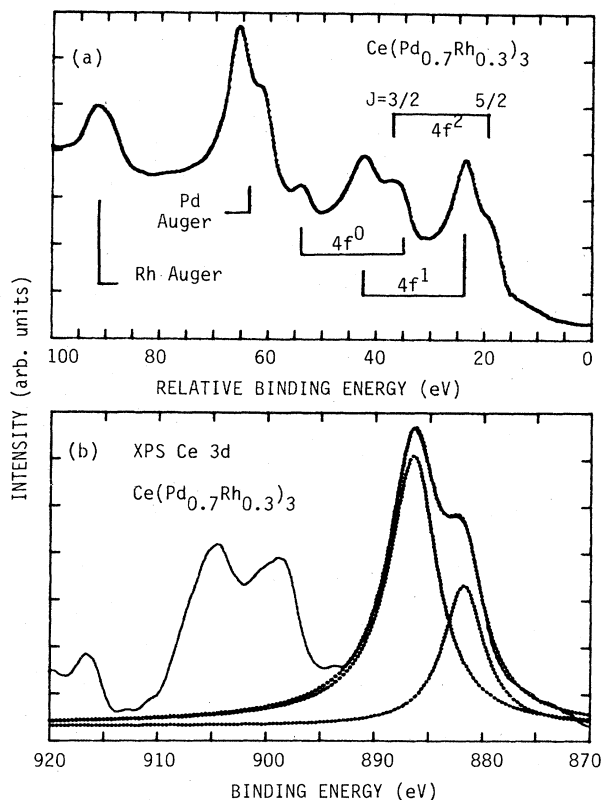
FIG. 1. (a) Photoemission spectrum for $Ce(Pd_{0.7}Rh_{0.3})_3$ showing Ce-derived $3d_{3/2}$ and $3d_{5/2}$ features, and Pd- and Rh-derived Auger features. (b) Truncated view of (a) showing deconvolution of Ce $3d_{5/2}$ emission into main feature and shakedown satellite. Background due to secondary electrons has been subtracted (see text).

The spectra were recorded using a system from Physical Electronics: the electron-energy analyzer was of the double-pass cylindrical mirror design, and the exciting radiation was the Mg K_α line (nonmonochromatized). The total resolution was 1 eV. The sample surfaces were checked for oxygen contamination by monitoring the x-ray-induced oxygen emission, since the O $1s$ level could not be used due to its overlap with the Pd $3p_{3/2}$ peak.

A typical spectrum over a wide energy range [Fig. 1(a)] exhibits, in addition to the Ce-derived $3d$ features, Rh- and Pd-derived Auger peaks. The double-peaked Pd Auger feature interferes with the mixed-valent component of the Ce $3d_{3/2}$ level. This spoils the measurement of mixed valence *per se*; however, we prefer to use the valence determined previously from L_{III} x-ray absorption measurements, since the latter type of measurements, unlike $3d$ XPS, is relatively free of final-state effects.[10,11] A background subtraction was required in order to obtain meaningful values for the relative intensities of the shakedown satellites. We determined the background in the following manner. First, an approximated polynomial was subtracted, and then a least-squares fit was made to the integrated area starting at the smaller-binding-energy side of the Ce $3d$ emissions. We note that different subtraction procedures may result in different values for the extracted intensities; however, the main goal in the present study was to be internally consistent throughout the series of compounds. In Fig. 1(b) is
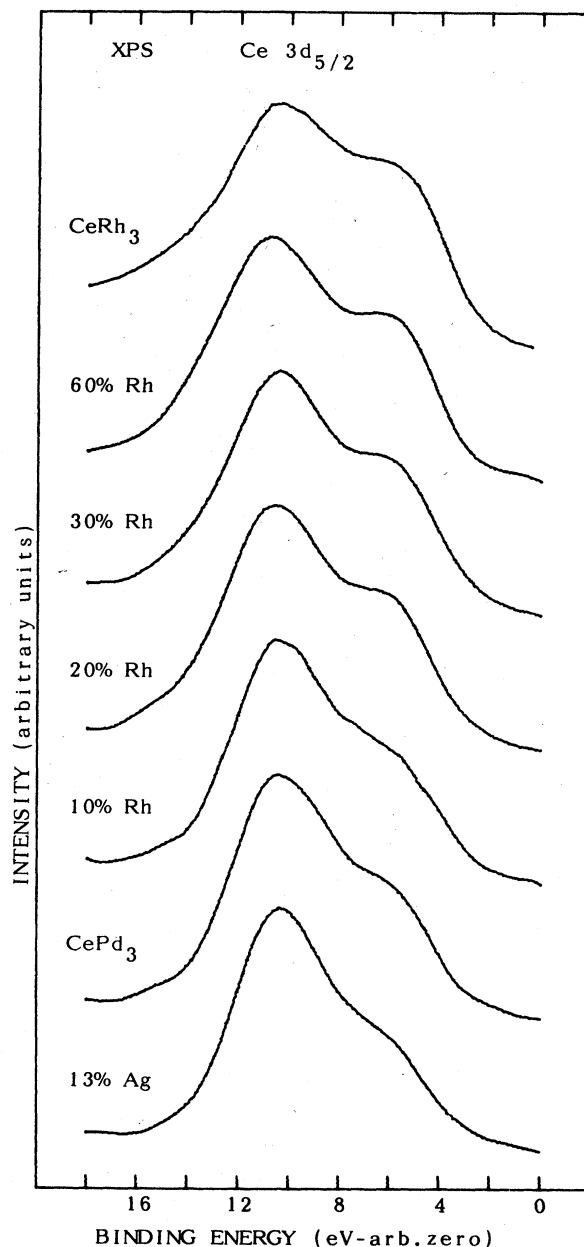

FIG. 2. Photoemission spectra after background subtraction, in region of Ce $3d_{5/2}$ emission, for series $Ce(Pd_{1-x}T_x)_3$, where $T = Ag$ or Rh.

shown an example of a fit obtained by using the Doniach-Sunjic function;[12] however, the fits deviated little from those of a Lorentzian, reflecting the smallness of the asymmetry index required.

In Fig. 2 are displayed the Ce $3d_{5/2}-4f^1$ (main line) and $4f^2$ (shakedown satellite) peaks after background subtraction. The shakedown satellite is the low-energy shoulder in Fig. 2. The bottom spectrum, which corresponds to the trivalent end of the series, has the smallest and the top spectrum ($CeRh_3$) has the largest satellite. The theory of Oh and Doniach[7] and the improved theory of Gunnarsson and Schönhammer[6] (GS) relate the shakedown intensity to
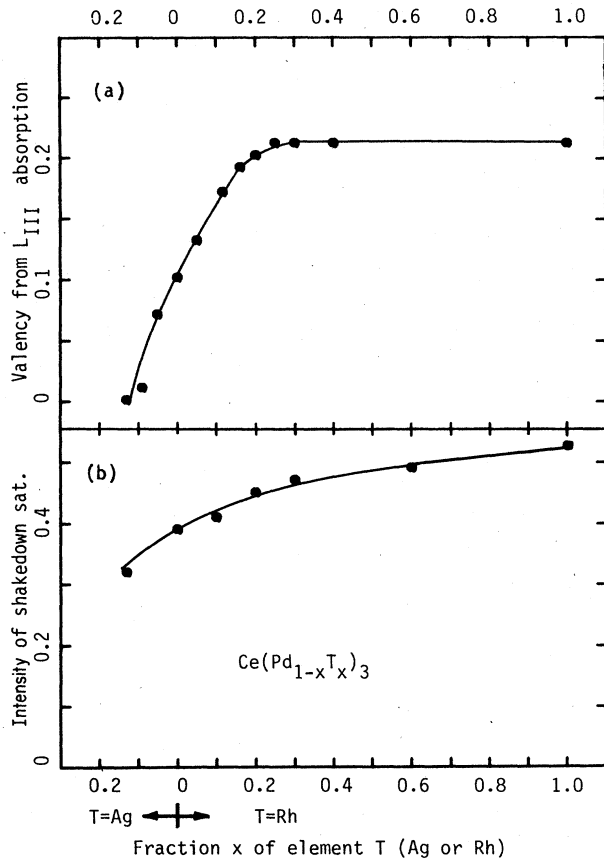
HYBRIDIZATION BETWEEN $4f$ AND CONDUCTION . . .

FIG. 3. (a) Valence, expressed in $4f$-hole count vs composition in the series $Ce(Pd_{1-x}T_x)_3$, as determined from L_{III} edge measurements (from Ref. 3). (b) Relative intensity of shakedown satellite in Ce $3d_{5/2}$ emission vs composition.

the hybridization energy Δ between the $4f$ and conduction electrons. Using the results from GS (Fig. 6 of Ref. 4) we obtain $\Delta \cong 0.2$ eV for the strongly mixed-valent end of the series. The (mixed) valence (from L_{III} edge studies)[3] and the (relative) intensity of the shakedown satellite are plotted as functions of composition in Figs. 3(a) and 3(b), respec-
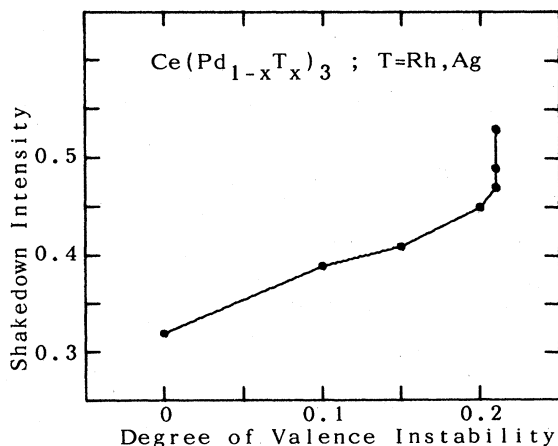
tively. As seen from Fig. 3, the shakedown intensity increases smoothly across the series, failing to exhibit any anomaly near $x_{Rh} = 0.2$, where the valence rather abruptly saturates. The nontracking of the valence with the shakedown intensity is exhibited more dramatically in Fig. 4, where these quantities are plotted one against the other. We note also that the shakedown satellite is sizeable even at the trivalent end of the series.

It has previously been pointed out[2] that the valence saturation is not likely to depend on the finer details in the hybridization, since systems with quite different electronic band structure exhibit similar behavior, i.e., fail to show valence instabilities corresponding to f counts of less than about 0.7. Hence, the explanation may be found in the atomic properties of Ce. The shakedown intensity is, in this study, found to decrease roughly linearly with increasing volume of the unit cell, Fig. 5, thereby indicating the relative insensitivity to electronic band structure. Wohlleben and co-workers[2] have developed a theoretical model based on thermodynamics which explains the valence saturation in Ce systems. Their model has two leading terms in the expression of the free energy; one is the elastic strain contribution, from the difference in the bulk moduli of the two configurations, which is positive, nearly independent of volume, has a maximum at valence $\simeq 3.4$, and tends to drive the system to integer valence. The other term is the contribution from configurational mixing. This term is negative, with a minimum near valence 3.2–3.3. Its magnitude is proportional to the hybridization energy Δ, which in turn increases linearly with decreasing volume in first order. At sufficiently small volume, the mixing contribution will dominate over the elastic strain contribution and then the valence will become trapped (saturated) at its minimum near valence 3.2–3.3. This model reproduces rather well the experimental results on low-volume Ce compounds[2(a)] and on elemental Ce under high pressure.[2(b)] Our present results are also consistent with this picture; in particular, we find that the hybridization energy Δ increases linearly with decreasing volume (Fig. 5), without any regard to whether the valence is saturated or not. However, we are not addressing here the validity of the initial assumptions in the derivation of the above-mentioned model.

A microscopic understanding of the saturation (and the

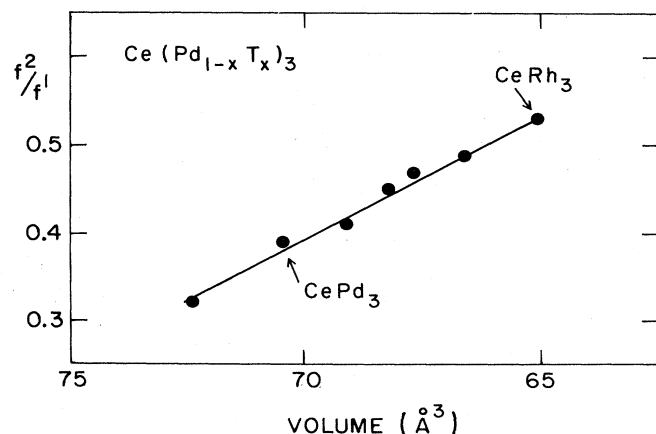FIG. 4. Relative intensity of shakedown satellite vs mixed valence ($4f$-hole count), see Fig. 3.

FIG. 5. Relative intensity of shakedown satellite vs volume of unit cell, see Fig. 3.

above model) may be based on the interplay of hybridization and spin-orbit effects.[2] Ordinarily, the degeneracy of the $4f$ level of Ce may be considered to lie between 2 and 6, depending on whether crystal-field effects are important—a degeneracy of 6 corresponding to the spin-orbit ground state and the neglect of crystal-field effects. However, hybridization will broaden the two ($J = \frac{5}{2}$ and $\frac{7}{2}$) spin-orbit levels which, in Ce, are separated by an energy of 0.27 eV. As the hybridization and hence the broadening of the levels becomes comparable to their separation, the two levels will mix, causing the degeneracy N to approach 14. This opening up of new hybridization channels, as expressed by the relation $\Delta \propto N$ (see e.g., Ref. 6), may slow the rate of change of valence with chemical pressure, viz., the observed valence-saturation effect.

In conclusion, we have measured the shakedown-satellite intensities (and therefore the hybridization between the $4f$ and conduction electrons) in a pseudobinary Ce-based system in which the electronic band structure varies continuously with composition. The findings are that the hybridization decreases roughly linearly with increasing volume of the unit cell, and no anomaly is seen where the degree of valence instability saturates rather abruptly. This lends support to the findings of the thermodynamical model of Wohlleben and coworkers,[2] in which the hybridization is related directly to the Ce volume. However, a comprehensive and microscopic theory is still needed to understand fully the anomalous saturation of the Ce valence.

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