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Photoemission studies of mixed valency: $Ce(Ag_{0.3}Pd_{0.7})_3$, $CePd_3$, and $CeRh_3$

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Photoemission studies of a Ce-compound system previously identified as spanning the entire mixed-valent range are presented. Valence-band spectra of $Ce(Ag_{0.3}Pd_{0.7})_3$, $CePd_3$, $CeRh_3$, and $LaPd_3$ suggest that Ce in $CePd_3$ is $3+$-like while in $CeRh_3$ it is more $4+$-like. However, resonant photoemission and partial-yield spectra show that Ce in $CeRh_3$ is not in a formal f^0 configuration as has been widely accepted.

Understanding mixed-valent behavior and the role of the $4f$ electron in Ce compounds presents scientists with a formidable and widely accepted challenge as evidenced by recent review articles.[1] The $Ce(Pd_{1-x}Rh_x)_3$-$Ce(Pd_{1-y}Ag_y)_3$ system is of particular interest in studying mixed valency because it is not complicated by extremely strong thermal phonon-valence fluctuation coupling as are other mixed valent systems (e.g., γ- and α-Ce). Motivated in part by a recent study of this system,[2] we have examined $Ce(Ag_{0.3}Pd_{0.7})_3$, $CePd_3$, $CeRh_3$, and (for comparison) $LaPd_3$, which have been assigned valences of $3.0+$, $3.45+$, $4.0+$, and $3.0+$, respectively.[2] This is the first ultraviolet photoemission spectroscopy (UPS) study of a Ce compound system which spans the entire $3+(4f^{1.0})$ to $4+(4f^{0.0})$ mixed valent range as determined by traditional lattice-volume-based methods. Our results demonstrate different f occupations than suggested by these methods.

Measurements of these Cu_3Au-structured compounds were carried out in an ultrahigh vacuum photoemission spectrometer at operating pressures of $\lesssim 6\times 10^{-11}$ Torr. Clean surfaces were obtained by fracturing the samples *in situ* and no evidence of contamination of the samples was observed during the experiments. Spectra were taken with a double-pass cylindrical mirror electron energy analyzer,[3] using synchrotron radiation at the Tantalus storage ring of the University of Wisconsin.

Our photoemission results for $LaPd_3$, $CePd_3$, and $CeRh_3$ are compared in Fig. 1 to the density-of-states (DOS) calculations of Moruzzi *et al.*[4] for the isomorphic alloys YPd_3, YRh_3, and $ZrRh_3$. Comparison of more extensive experimental spectra for $CePd_3$ and $LaPd_3$ at photon energies between 10 and 70 eV showed that all spectral features within 3 eV of the Fermi level E_F were indistinguishable within experimental resolution. Therefore the spectra of Fig. 1 reveal features which are primarily non-f-related, i.e., they are Rh or Pd $4d$ derived. In panel (a) of Fig. 1 we indicate three Pd-derived features[4] in the calculated DOS of YPd_3 which are also evident in the experimental spectra of $LaPd_3$ and $CePd_3$. This comparison of $CePd_3$ to $LaPd_3$ and experiment to calculation shows that there is no measurable evidence for significant $4f$ electron promotion or for other conduction band perturbations due to $4f$-$4d$ hybridization.

In panel (b) of Fig. 1 we show that for $CeRh_3$ the Ce $4f$ electron *does* affect the valence-band states and that the experimental spectra are in better agreement with the DOS of $ZrRh_3$ than with that of YRh_3 (Y is formally $3+$, Zr is $4+$). Again, arrows indicate the Rh $4d$-derived features in $CeRh_3$, YRh_3, and $ZrRh_3$. As shown, there are only two $4d$ structures in the calculated DOS of YRh_3, the third being above E_F. In $ZrRh_3$, with one more electron, the third feature is broadened and the Fermi level cuts through it, leading to a $4d$ shoulder in the DOS.[4] Experimentally, a clear shoulder is observed near E_F which suggests an extra filling of the Rh $4d$ states (no experimental comparison to $LaRh_3$ was made because, significantly, it does not have the Cu_3Au structure). While previous studies[5] have shown $4f$ emission cutoff at the Fermi level, this represents the first direct photoemission evidence for $4f$-to-conduction-d-band charge transfer in a Ce compound.

Additional insight concerning the $4f$ electron in this system can be gained through the use of resonant photoemission.[6] In Fig. 2 we show spectra

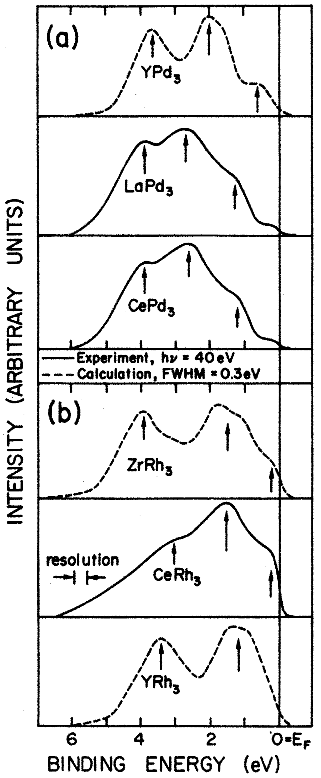

FIG. 1. Background-subtracted photoemission spectra for $LaPd_3$, $CePd_3$, and $CeRh_3$ compared to calculations from Ref. 4. The calculated densities of states have been Gaussian-broadened to account for the experimental resolution.

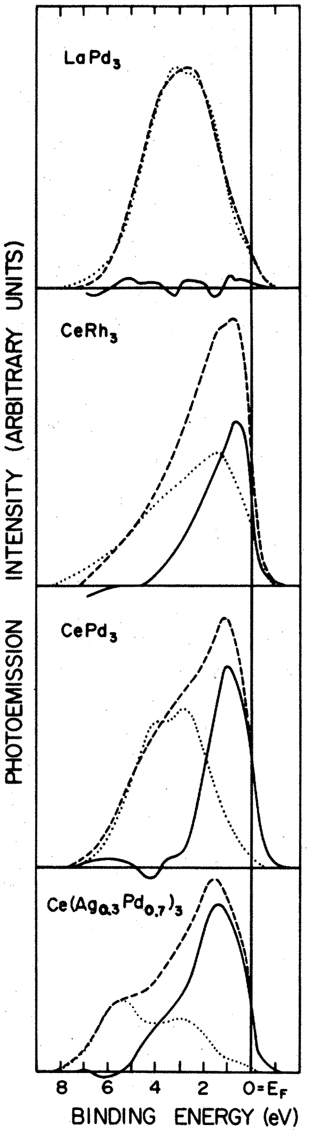

FIG. 2. Background-subtracted photoemission spectra (resolution ~0.8 eV) taken near (dashed lines) and before (dotted lines) the $4d \rightarrow 4f$ resonance. As discussed in the text, the difference spectra (solid lines) highlight the $4f$ emission. The peak of the f-related feature shifts from ~1.3 eV in $Ce(Ag_{0.3}Pd_{0.7})_3$ to ~0.9 eV in $CePd_3$ to ~0.5 eV in $CeRh_3$. The peak near 5.4 eV in $Ce(Ag_{0.3}Pd_{0.7})_3$ is due to the Ag $4d$ bands.

taken before the $4d \rightarrow 4f$ resonance (~113 eV), those taken near the resonance (~119 eV), and difference curves formed by subtracting the preresonance from the resonance spectra. For completeness, we include analogous data for $LaPd_3$ taken before (~107 eV) and near (~113 eV) its $4d \rightarrow 4f$ "resonance" energy. Prior to the peak in the $4d$ absorption, the decay of the resonantly excited $4d^9 4f^{n+1}$ configuration enhances the normal (but small) $4f$ photoemission signal. By scaling the preresonance spectra to match the resonance spectra in the high-binding-energy region (farthest away from the f level) and then taking the difference of these two spectra, we highlight the f-derived emission. This scaling procedure is most accurate for materials with distinct features far from the f emission. It is thus least accurate for $CeRh_3$ as can be seen in Fig. 2. Unlike the spectrum of $LaPd_3$, those of the Ce-containing compounds, *including* $CeRh_3$, show $4f$ emission near E_F. The observed shift of these $4f$ features is consistent with a decreasing f occupation in both promotion and band models. Our spectra for $CePd_3$ agree with those of Allen *et al.*,[5] who suggested that the large width of the $4f$-related feature may be due to hybridization. We have found the $4f$ emission of *all* of these compounds to be significantly broader than that observed in our previous studies of other Ce containing compounds [these include $CeAl_2$, CeS, CeSe, CeTe, CeN, CeP, CeAs, CeBi, $CeSn_3$, CeH_2, CeH_3, γ-Ce, α-Ce, and $CeSi_2$

(Refs. 7–9)]. The broadest $4f$ feature is in the Ag compound and its high binding energy shoulder is reminiscent of a localized f-hole final-state feature typical of other Ce^{3+} compounds.[7] However, the interpretation of this feature is complicated by the possibility of local environmental effects. The shape of these $4f$ features suggests that the $4f$ occupation is about equal for $Ce(Ag_{0.3}Pd_{0.7})_3$ and $CePd_3$ and is greater than that assigned by lattice-volume measurements. The most striking conclusion is that Ce *is not* in a formal $4f^0$ atomic configuration in $CeRh_3$, at least in the surface region to which our measurements are most sensitive. Our partial yield results, discussed below, argue that this conclusion should be extended to the bulk.

To further explore the question of valency we have examined the fine structure associated with the partial photoelectric yield in the vicinity of the Ce $4d$ core excitation. Multiplet structure in the photoyield has been effectively modeled[10] by considering the exchange splitting of the $4d^9 4f^{n+1}$ excited state formed by the creation of a $4d$ hole. This structure provides a fingerprint of the f occupation and avoids the complication of satellite features which plague core-level identifications.[11] Figure 3 shows the yield spectra for electrons with a kinetic energy of 4 eV. The lower portion emphasizes the fine structure and shows that the yields of $Ce(Ag_{0.3}Pd_{0.7})_3$ and $CePd_3$ are practically indistinguishable. (We further note that the yield spectra of these two compounds are very similar to that of $CeAl_2$ which is generally accepted as having a localized f^1 configuration.[8]) However, by comparison to $LaPd_3$ we see that the partial yield of $CeRh_3$ has *both* f^0-like and f^1-like features. We wish to stress that, because of our choice of accepting electrons with such low kinetic energies, these results are overwhelmingly representative of the bulk and support the conclusions drawn from Fig. 2.[11]

There have been a number of studies questioning the conventional lattice-volume-based valence assignments in Ce compounds. General arguments based upon thermodynamic properties[12] and upon lattice systematics of the other rare earths[13] can be found in the literature. Band theoretical[14] and experimental investigations[15] have largely focused on the temperature-dependent γ-α phase transition in Ce and have found that the f occupation changes far less than indicated by the lattice-volume-derived value of 0.7 electron. The UPS results presented here on a series of isostructural compounds carry a very clear message on the Ce volume-valence coupling. On going from the "hard" $4f^1$ compound $Ce(Ag_{0.3}Pd_{0.7})_3$ to the one-half volume collapsed compound $CePd_3$, we find little evidence for $4f$ depopulation. Only after the Ce atoms are well through the "mixed-valent" volume range in $CeRh_3$ do we see evidence for $4f$-to-$4d$ charge transfer and even then we see substantial $4f$ character. Thus our work indicates that the volume collapse and concomitant changes in susceptibility, resistivity, and specific heat[2] are not directly related to a loss of f character.

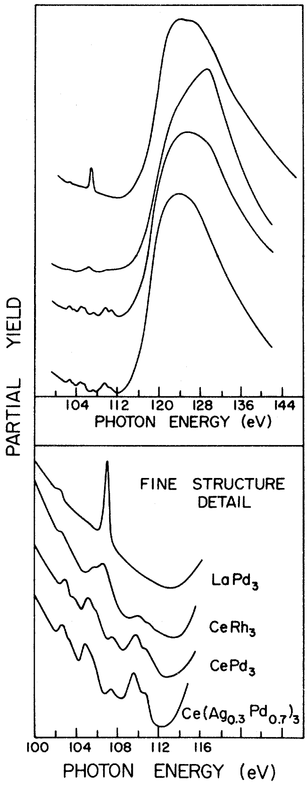

FIG. 3. Partial photoelectric yield spectra for $Ce(Ag_{0.3}Pd_{0.7})_3$, $CePd_3$, $CeRh_3$, and $LaPd_3$ shown in order of reported f occupancy. As discussed in the text, the low-energy fine structure is characteristic of the f occupation. The spectrum for $LaPd_3$ has been shifted to higher binding energy by ~5 eV for clarity.

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[1] See, for example, A. C. Hewson, J. Magn. Magn. Mater. 12, 83 (1979) and J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).

[2] T. Mihalisin, P. Scoboria, and J. A. Ward, Phys. Rev. Lett. 46, 862 (1981).

[3] G. Margaritondo, J. H. Weaver, and N. G. Stoffel, J. Phys. E 12, 662 (1979).

[4] V. L. Moruzzi, A. R. Williams, and C. D. Gelatt, *Calculated Electronic Properties of Ordered Alloys* (in press).

[5] J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagström, Phys. Rev. Lett. 46, 1100 (1981).

[6] See, for example, W. Lenth, F. Lutz, J. Barth, G. Kalkoffen, and C. Kunz, Phys. Rev. Lett. 41, 1185 (1978); A. Zangwill and P. Soven, *ibid.* 45, 204 (1980).

[7] A. Franciosi, J. H. Weaver, N. Martensson, and M. Croft, Phys. Rev. B 24, 3651 (1981).

[8] M. Croft, J. H. Weaver, D. J. Peterman, and A. Franciosi, Phys. Rev. Lett. 46, 1104 (1981). The partial yield of $CeAl_2$ was obtained under the same experimental conditions.

[9] A more detailed report reviewing all of our photoemission studies of Ce is in progress.

[10] J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, Phys. Rev. Lett. 26, 1521 (1971).

[11] G. Krill, J. P. Kappler, A. Meyer, L. Abedli, and M. F. Ravet, J. Phys. F 11, 1713 (1981). These authors also discount surface effects.

[12] B. Johansson, Philos. Mag. 30, 469 (1974); F. R. de Boer, W. H. Dijkman, W. C. M. Mattens, and A. R. Miedema, J. Less-Common Met. 64, 241 (1979).

[13] See, for example, D. K. Wohlleben in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 1, and references therein.

[14] W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 23, 1266 (1981).

[15] U. Kornstädt, R. Lässer, and B. Lengeler, Phys. Rev. B 21, 1898 (1980); D. R. Gustafson, J. D. McNutt, and L. O. Roellig, Phys. Rev. 183, 435 (1969).