4f-Derived Resonant Photoemission in the Early Rare Earths: Possible Evidence for Localized Screening Channel

R. D. Parks, S. Raaen,[a] M. L. denBoer, and Y.-S. Chang
Department of Physics, Polytechnic Institute of New York, Brooklyn, New York 11201

and

G. P. Williams
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

(Received 8 November 1983; revised manuscript received 12 March 1984)

Photoemission studies of $RE\mathrm{Ru}_2$ and $RE\mathrm{Pd}_2$ (RE = Ce, Pr, Nd) reveal two 4f-derived features with an energy separation of ~ 2.5 eV, which move in parallel to larger binding energies in going from Ce to Pr to Nd. These results, which are at variance with predictions of Anderson-model treatments based on the large–orbital-degeneracy approximation, are compatible with the treatments of Liu and Ho and of Riseborough, who distinguished between the two peaks on the basis of their screening geometries.

PACS numbers: 78.70.Dm, 71.90.+q

A major puzzle in the mixed-valence problem is the origin of the 4f instability in cerium-based systems. Mixed-valence behavior (nonintegral 4f occupancy) in Sm-, Eu-, Tm-, and Eu-based systems appears to be well understood in terms of the promotional (or Anderson) model, which describes the ground state as an admixture of the states $4f^nc^m$ and $4f^{n+1}c^{m-1}$, where c denotes a conduction electron (see, e.g., Lawrence, Riseborough, and Parks[1]). An early indication of the inadequacy of such a description for mixed-valent (MV) Ce-based systems was Johansson's estimate,[2] based on cohesive energy arguments, that the energy difference between the $4f^15d^16s^2$ and $4f^05d^26s^2$ configurations in metallic cerium is 2–3 eV, which implies that at thermal energies there can be negligible occupancy of the $4f^05d^26s^2$ state. Similar conclusions, based on cohesive energy arguments by de Boer *et al.*,[3] apply to a wide class of Ce-based intermetallics. Equally provocative are the results of 3d x-ray photoemission spectroscopy[4] and L_{III} absorption[5-7] experiments on a large number of Ce-based intermetallics, thought formerly to be tetravalent ($4f^05d^26s^2$) or nearly tetravalent on the basis of lattice-constant measurements, which indicate a formal valence of only ~ 3.15–3.3 for these materials, corresponding to an f count of 0.85–0.7.

In order to gain further insight into the cerium problem, we have performed resonant photoemission experiments on the moderately strongly MV system CePd_3 (valence ~ 3.1)[4,5] and the strongly MV system CeRu_2 (valence ~ 3.2–3.3),[4,5] along with their (integral valent) Pr and Nd homologs. The experiments were performed on Station U14 of the 750-MeV vacuum ultraviolet ring at the National Synchrotron Light Source (NSLS). A plane-grating monochromator, together with a double-pass cylindrical-mirror analyzer, gave a combined resolution (electrons plus photons) of 0.4–0.5 eV at 100 eV and 0.5–0.6 eV at 120 eV. Clean sample surfaces were prepared by fracturing the samples *in situ* in the measuring chamber, where the nominal pressure was 1×10^{-10} Torr.

In order to isolate the 4f-derived emission from that of the conduction band, photoemission spectra were taken at the giant 4d–4f (Fano) resonance[8,9] ($\hbar\omega$ = 122, 124, and 128 eV for Ce-, Pr-, and Nd-based systems, respectively), which enhances the 4f emission via the excitation $4d^{10}4f^n \rightarrow 4d^94f^{n+1} \rightarrow 4d^{10}4f^{n-1}[c]$, where $[c]$ denotes the screening electron for the final 4f hole state. This resonance is shown for CePd_3 in the constant-initial-state (CIS) spectrum in Fig. 1. Shown also is the CIS spectrum for LaPd_3 which shows a much smaller peak (at $\hbar\omega$ ~ 117 eV) resulting from the weaker excitation $4d^{10}4f^0 \rightarrow 4d^94f^1 \rightarrow 4d^{10}4f^0\text{-}c^*[c]$, where c^* denotes the final conduction-band hole state. The two CIS spectra were taken at binding energies of 1.5 eV for CePd_3 and 4.0 eV for LaPd_3, the latter energy falling within the Pd 4d band. CIS spectra taken for other binding energies in the range 1–4 eV in LaPd_3 are similar to the one shown in Fig. 1. The steep photon energy dependence in the energy range 95–110 eV for both spectra reflects the energy dependence of the Pd-derived 4d emission.

The 4f-derived photoemission spectra for $RE\mathrm{Ru}_2$ and $RE\mathrm{Pd}_3$, obtained by subtracting the off-resonance spectra ($\hbar\omega$ = 112, 114, and 120 eV for Ce, Pd, and Nd, respectively) from the on-resonance

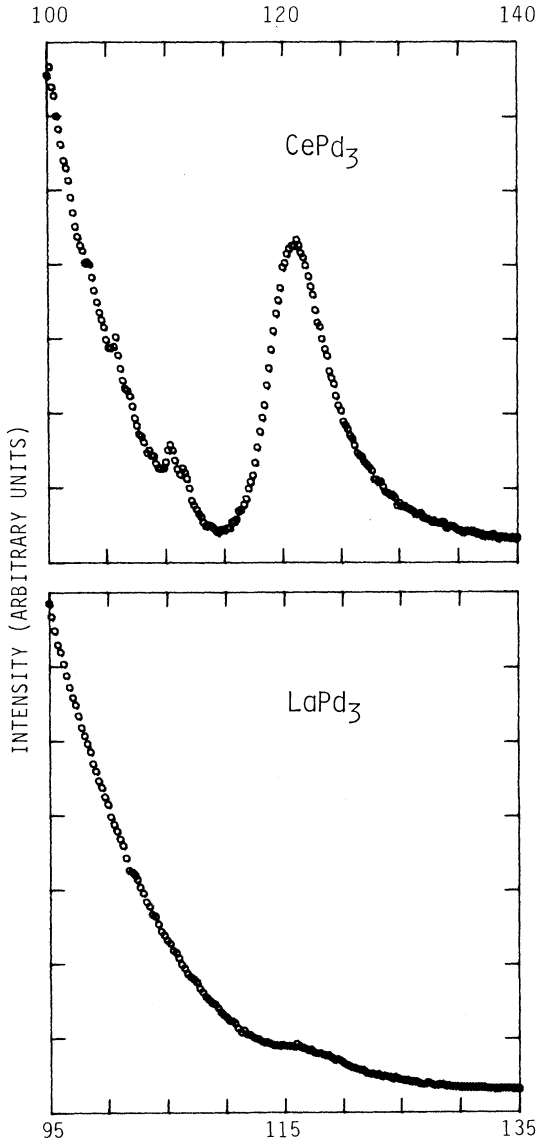

FIG. 1. Constant-initial-state (CIS) spectra for $CePd_3$ and $LaPd_3$, taken at the binding energies 1.5 and 4.0 eV, respectively.

spectra, and also subtracting the background due to secondary electrons, are shown in Figs. 2 and 3, respectively. The spectra for $CeRu_2$ and $CePd_3$ are quite similar to those obtained by other investigators, who also interpret them as being dominated by $4f$ emission.[10,11] The off-resonance spectra for the REPd$_3$ samples were normalized to correct for the photon energy dependence of the Pd-derived $4d$ emission observed in $LaPd_3$ (Fig. 1), this being necessary to establish definitively the presence of the weaker, large-binding-energy feature in $CePd_3$ and $PrPd_3$. A similar correction was deemed unnecessary for the RERu$_2$ series, because of the relative flatness and smallness of the off-resonance spectra (see, e.g., Ref. 10).

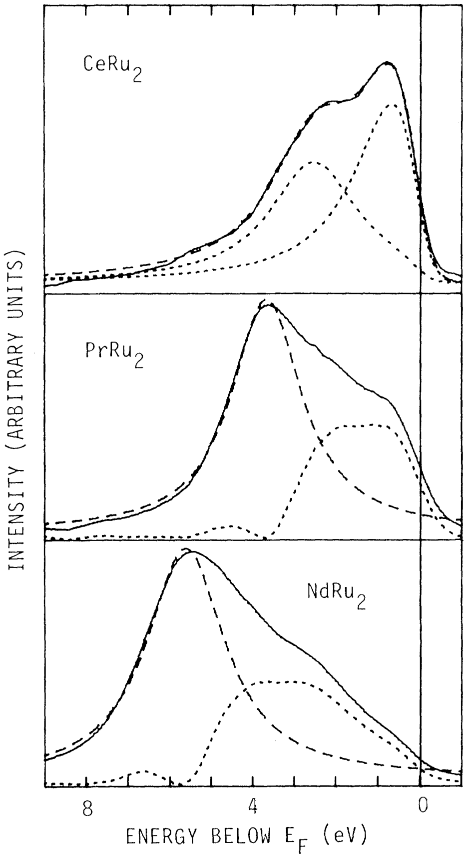

FIG. 2. Solid lines: $4f$-derived energy distribution curves for $CeRu_2$, $PrRu_2$, and $NdRu_2$, obtained by procedure discussed in text; broken lines: fits to the two spectral features as discussed in text.

The key result of the present study is the finding that the smaller-binding-energy feature (i.e., closer to E_F) remains at a fixed energy separation from the larger-binding-energy feature, and that the two features move together as the f level moves further from E_F in going from Ce to Pr to Nd, as illustrated in Fig. 4. The positions of the two features were determined in the following manner. For $PrRu_2$, $NdRu_2$, and $NdPd_3$, a Lorentzian was fitted to the larger binding-energy peak and the second feature was obtained by subtracting the Lorentzian from the total spectrum (Figs. 2 and 3), a procedure similar to that used by other investigators.[12] For $CeRu_2$, $CePd_3$, and $PrPd_3$, the smallness of the larger-binding-energy feature prevented this approach; hence, the alternative procedure of fitting Lorentzians to both features was employed,

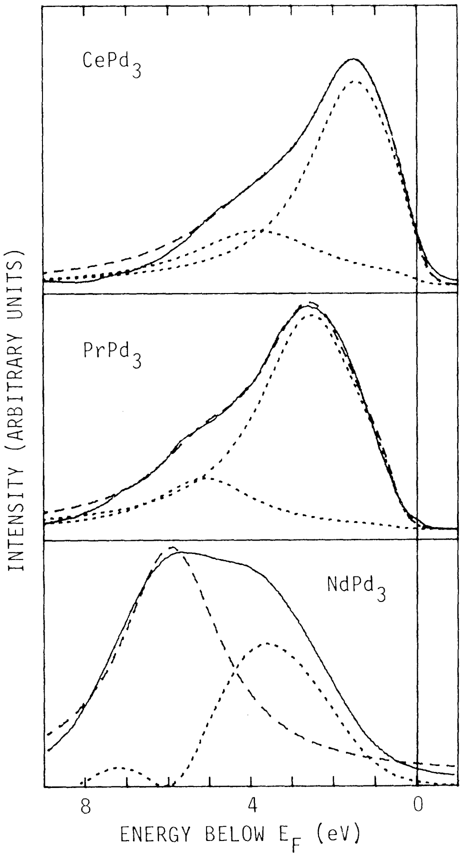

FIG. 3. Solid lines: $4f$-derived energy distribution curves for CePd$_3$, PrPd$_3$, and NdPd$_3$; broken lines: see Fig. 2 caption and text.

wherein a Fermi cutoff was convoluted with the instrumental resolution function. The somewhat poorer fit to the higher-binding-energy feature in the Nd samples is due presumably to the multiplet splitting of the $4f$ state, which has the effect of distorting and broadening the higher-energy side of the peak (see, e.g., Lang, Baer, and Cox[13]). The locations of the two features, plotted in Fig. 4, correspond to the mean energies of the non-Lorentzian fits and the peak locations of the Lorentzian fits. In the case of CeRu$_2$ it is possible only to bracket the smaller-binding-energy peak between 0 and 0.6 eV, because of the closeness of the peak to E_F, and in view of the finite instrumental resolution.

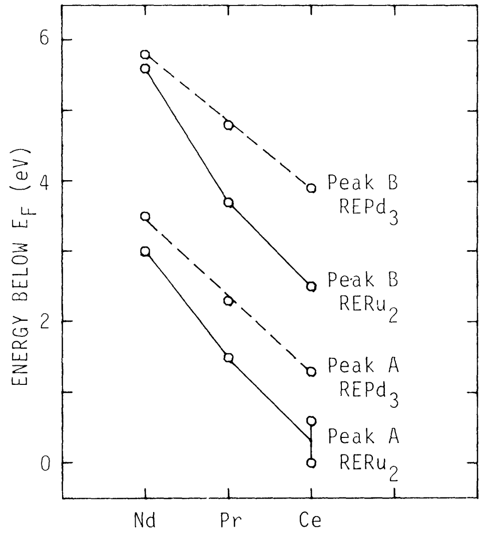

FIG. 4. Energy positions of the two f-derived features in RERu$_2$ and REPd$_3$ (RE = Ce, Pr, Nd). Peaks A and B refer to the feature closer to and that further from E_F, respectively.

Treatments of the Anderson model[14] or Anderson lattice model[15] in the limit of large orbital degeneracy produce a feature in the f spectral density centered at E_F, which is expected to decrease in intensity, but not move, as the f level is moved away from E_F. This is at variance with the present results, which demonstrate that the two f-derived features are locked together and move in unison as the f level is moved away from E_F. On the other hand, the observed behavior is consistent with an idea presented by Liu and Ho[16] and recently carried a step further by Riseborough.[17] In these approaches the two f-derived features are differentiated by their different screening geometries, the larger-binding-energy features corresponding to an f hole screened conventionally by an itinerant electron and the smaller-binding-energy feature to an f hole screened by a radially localized electron, such localization being induced by the large Coulomb attraction generated by the $4f$ hole. Riseborough's approach is to modify the Anderson-model Hamiltonian by adding a term representing the Coulomb attraction between the $4f$ electrons and the conduction electrons, and calculating the resulting f spectral density in the low-density (of conduction electrons) approximation. The new physics emerging from the latter approach is the finding that hybridization is necessary for the required localization. This explains the decrease in the size of the locally screened feature in going from left to right in the rare-earth series, due to the lanthanide contraction of the $4f$ shell.[18,19]

In view of the present results we speculate that mixed valence can occur in Ce-based systems only if the $4f$ holes are locally screened, the corresponding 2–3-eV Coulomb energy gain being sufficient to overcome Johansson's energy barrier for $4f$ hole formation discussed above. Moreover, the contraction of a valence electron, probably mainly of $5d$ character, may explain the anomalously large lattice contraction observed in mixed valent Ce-based systems.[1,5,6]

While the concept of localized screening may constitute a zero-order explanation of the photoemission spectra observed for Ce-based systems, the sensitivity of the signature of the $4f$-derived spectra to the nature of the solid-state matrix suggests the inadequacy of approximating the hybridization merely by a scalar number. Band-structure effects must be considered, and, perhaps as well, nearest-neighbor ligand effects as discussed by Fujimori.[20]

We are indebted to Peter Riseborough for helpful discussions and communication of results prior to publication, and to Jon Lawrence for playing the useful role of devil's advocate. This work supported in part by the U.S. Department of Energy under Contract No. DE-AC02-81ER10862 and in part by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

---

[a] Present address: Physics Department, Brookhaven National Laboratory, Upton, N.Y. 11973.

[1] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[2] B. Johansson, Philos. Mag. **30**, 469 (1974).

[3] F. R. de Boer, W. H. Dijkman, W. C. M. Mattens, and A. R. Miedema, J. Less-Common Met. **64**, 241 (1979).

[4] J. C. Fuggle, F. U. Hillebrecht, Z. Zolnierek, R. Lässer, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983), and references cited therein.

[5] K. R. Bauchspiess, W. Boksch, E. Holland-Moritz, H. Launois, R. Pott, and D. Wohlleben, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1982), p. 417.

[6] R. D. Parks, S. Raaen, M. L. denBoer, V. Murgai, and T. W. Mihalisin, Phys. Rev. B **28**, 3556 (1983).

[7] S. Raaen and R. D. Parks, Solid State Commun. **48**, 199 (1983).

[8] L. I. Johansson, J. W. Allen, T. Gustafsson, I. Lindau, and S. B. Hagström, Solid State Commun. **28**, 53 (1978).

[9] W. Lenth, F. Lutz, J. Barth, G. Kalkoffen, and C. Kunz, Phys. Rev. Lett. **41**, 1185 (1978).

[10] D. J. Peterman, J. H. Weaver, M. Croft, and D. T. Peterson, Phys. Rev. B **27**, 808 (1983).

[11] J. W. Allen, S.-J. Oh, M. B. Maple, and M. S. Torikachvili, Phys. Rev. B **28**, 5347 (1983).

[12] J. M. Lawrence, J. W. Allen, S.-J. Oh, and I. Lindau, Phys. Rev. B **26**, 2362 (1982).

[13] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F **11**, 121 (1981).

[14] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983), and Phys. Rev. B **28**, 4315 (1983).

[15] S. Doniach, private communication.

[16] S. H. Liu and K.-M. Ho, Phys. Rev. B. **26**, 7052 (1982).

[17] P. S. Riseborough, private communication.

[18] F. U. Hillebrecht and J. C. Fuggle, Phys. Rev. B **25**, 3550 (1982).

[19] S. Raaen and R. D. Parks, Phys. Rev. B **27**, 6469 (1983).

[20] A. Fujimori, Phys. Rev. B **28**, 2281 (1983).