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Brief Reports

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Anomalous saturation of mixed valence in cerium-based systems as studied by x-ray absorption

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The mixed valence of cerium-based metallic systems, as determined, for example, by x-ray-absorption experiments, never rises above 3.2–3.3. The L_{III} absorption-edge studies we report here show that this saturation effect occurs abruptly as a function of lattice constant (or composition) in the pseudobinary system $\mathrm{Ce(Pd_{1-x}Rh_x)_3}$, in which it is possible to vary both continuously and rapidly the electronic properties. The saturation anomaly (at the valence 3.21) occurs at $x \approx 0.2$, the composition where anomalous saturation effects have been previously observed in the magnetic susceptibility, electronic specific heat, and electrical resistivity. The values of the latter quantities at $x \approx 0.2$ suggest a valency of ~ 4, when interpreted within the promotional model.

X-ray absorption measurements, particularly of the L_{III} edge, provide a convenient and direct method of determining the mixed valence of rare-earth compounds. In the presence of a $4f$ hole, the L_{III} edge, which represents the excitation of an electron from the $2p_{3/2}$ core level into the conduction band, is shifted by approximately 10 eV to higher binding energy.[1] Hence the ratio of the two intensities provides a direct determination of the mixed valence, i.e., the ratio of the $4f^n$ and $4f^{n-1}$ components in the ground state. In mixed-valent Eu-, Sm-, Tm-, and Yb-based systems, values of the valence have been observed which span the full range of allowed values. On the other hand, the mixed valence in metallic Ce-based compounds, as measured by L_{III} absorption, has never been observed to be larger than 3.2–3.3, corresponding to $f^0/(f^1+f^0) = 0.2\text{–}0.3$.[2]

The purpose of the present study was to examine the onset of the above saturation effect in a Ce-based system, in which it is possible to vary continuously those properties, e.g., electronic band structure, which might be expected to influence the degree of the $4f$ instability. The system chosen was $\mathrm{Ce(Pd_{1-x}T_x)_3}$, where $T=\mathrm{Ag}$ or Rh. For $x_{\mathrm{Ag}} \geq 0.13$, the behavior reflects a stable $4f$ configuration (trivalent state), whereas decreasing x_{Ag} from 0.13 to 0, followed by increasing x_{Rh} from 0 to 0.2, leads to a continuous increase in the degree of $4f$ instability, as evidenced in the magnetic susceptibility, electronic specific heat, and electrical conductivity.[3,4]

The intermetallic compounds for the x-ray absorption study were prepared by arc melting in an inert atmosphere, followed by annealing at 800 °C for five days in order to ensure homogeneity. The material was then powdered and hermetically sealed in a suitable tape sandwich, the thickness of the resulting sample falling in a region for which the edge spectra were established experimentally to be thickness independent. The experiments were performed in transmission at the Cornell University synchrotron radiation facility, CHESS, with the use of x rays emitted by the storage ring, CESR, operating at 5.3 GeV. A monochromator using two Si(111) crystals offset by 8 cm and mounted 11 m from the source gave a resolution (half-width at half maximum) of about 0.7 eV at the Ce L_{III} edge. The L_{III} edge spectra are shown in Fig. 1.

The L_{III} spectra in Fig. 1 reveal a monotonic growth of the satellite edge feature as one traverses the range of compositions indicated. Not shown in Fig. 1 are the spectra for 25 and 100 at.% Rh, which are visually similar to those for 30 and 40 at.% Rh. In the promotional model picture,[1] the lower-energy L_{III} edge should occur in Ce-based systems at the energy of the final state $2p^*4f^15d^26s^2$, and the higher-energy edge at the energy $2p^*4f^05d^36s^2$, where $2p^*$ denotes a $2p$ core hole. In order to extract the ratio of the intensities of the two edges, the following method was employed. An analytic function was fitted to the 13-at.% Ag spectrum, for which the satellite edge is assumed to be zero, i.e., negligibly small. A Gaussian with a linearly decreasing tail on the high-energy side imposed on a background with a step discontinuity at the peak maximum fits this spectrum quite well. This function was then fitted to each of the peaks in the other samples in this series. The background step and slope were constrained to be the same throughout the series to eliminate effects due to sample nonuniformi-

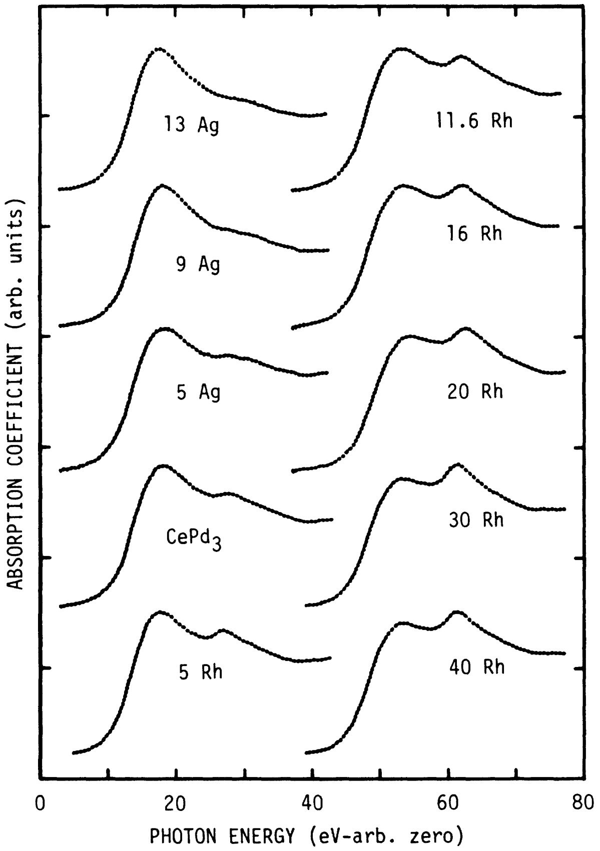

FIG. 1. Cerium L_{III} absorption spectra for the pseudobinary series $\mathrm{Ce(Pd}_{1-x}T_x)_3$, where $T=\mathrm{Ag}$ or Rh. Values of x are expressed in precentages. Only relative energies as shown on the abscissa. The primary (lower-energy) edge occurs near 5.724 eV.

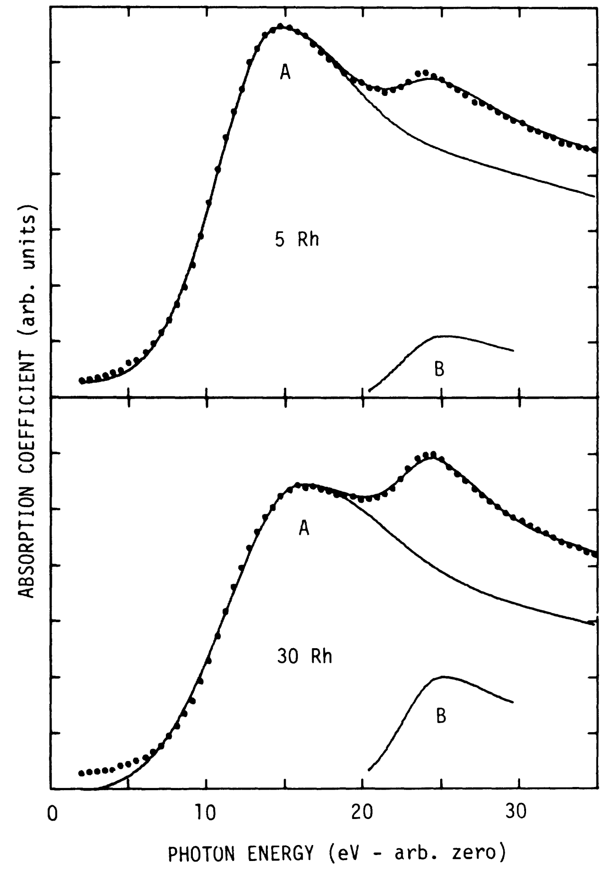

FIG. 2. Double-peak structure of the Ce L_{III} absorption edge in $\mathrm{Ce(Pd_{0.95}Rh_{0.05})_3}$ and $\mathrm{Ce(Pd_{0.70}Rh_{0.30})_3}$, modeled by a peak A and a secondary peak B, using the method described in text.

ties, etc.; however, the width of the Gaussian was allowed to vary. The contribution of each peak was estimated by integrating the fitting function from 8 eV below to 8 eV above the maximum. The integration was truncated above the edge since small errors in determining the high-energy tail would spoil the peak intensity determination if the integration were extended to high energy. Representative fits for two of the spectra (5 and 30 at.% Rh) are shown in Fig. 2. The A edge function has been analytically continued beyond the fitting range in order to exhibit the edge shape.

In Fig. 3 we exhibit the relative size of the f^0 edge $B/(A+B)$, determined by the fitting procedure discussed above. The compositions from left to right are $x=100$, 40, 30, 25, 20, 16, 11.6, 5 at.% Rh, 0, 5, 9, and 13 at.% Ag. The lattice constants for $\mathrm{CePd_3}$ and $\mathrm{Ce(Pd_{1-x}Rh_x)_3)}$ were taken from Ref. 4, and those for $\mathrm{Ce(Pd_{1-x}Ag_x)_3}$ from Ref. 5. As seen in Fig. 3 there is an abrupt arresting of the growth of the satellite with increasing Rh concentration at $x_{\mathrm{Rh}} \approx 20\%$. The observed saturation value 0.21 corresponds to a formal valence of 3.21. The discrepancy between this value and the value 3.29 reported by Bauchspiess *et al.* for $\mathrm{CeRh_3}$ presumably reflects differences in the method used to fit the edge spectra in Ref. 2 and the present work, since the spectrum for $\mathrm{CeRh_3}$ in Ref. 2 is visually similar to the spectra obtained in the present work. The method used in Ref. 2 to fit edge spectra gives consistently larger values than our method; however, any method which is consistent for all samples would produce the shoulder in Fig. 3.

It has been objected that final-state effects,[6] e.g., shake-up or shake-down processes, might affect or even dominate the ratio of the L_{III} edge features in Ce-based systems, and hence that the ratio does not accurately reflect the $4f$ ground-state occupation. More recently, it has been concluded, on the basis of L_{III} edge studies of a number of Ce-

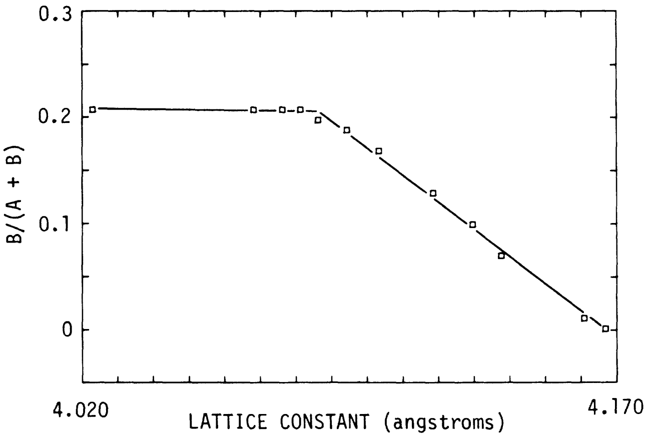

FIG. 3. Relative size of the secondary edge B, given by $B/(A+B)$, where A and B are the intensities of the two edge features, vs lattice constant for $\mathrm{Ce(Pd}_{1-x}T_x)_3$; see text for method of analysis and identification of data points. The solid lines are merely visual aids.

based intermetallics, together with their La and/or Pr isomorphs, that such final-state effects play a minor role, and that the $L_{\rm III}$ edge spectrum provides a reasonably accurate value of the mixed valency.[7] On the basis of Ref. 7, we estimate that final-state effects can produce uncertainties of at most ±10% in the quantity $V-3$, where V is the apparent valence based on the observed edge ratio.

The saturation anomaly in the valence at $x_{\rm Rh}\approx 20$ at.% (Fig. 3) is obviously related to the saturation anomalies previously observed[3,4] at the same composition in the magnetic susceptibility, electronic specific heat, and electrical resistivity. The saturation values of the latter properties at $x_{\rm Rh}\approx 20$ at.%, when interpreted within the promotional model, suggest a valence of about 4. Hence it was natural to assume that the saturation effect heralded the arrival of cerium at its maximum possible valence.[3,4]

The task of the theory is to explain why the valence of mixed-valent Ce-based systems is dramatically smaller than that suggested by the lattice constant and magnetic susceptibility, and how it can saturate abruptly as reported in the present experiment. A recent calculation by Fujimori[8] may provide a clue to the explanation. The calculation, which is based on a $\rm CeO_8$ cluster modeling of $\rm CeO_2$, finds strong hybridization between the $4f$ electrons and the O-derived $2p$-ligand states. This leads to a ground state which is a mixture of two configurations: $4f^0$ and spin-singlet totally symmetric $4f^1$-O $2p$-hole states.[9] Fujimori postulates that the same mechanism may be operative in α-Ce and mixed-valent Ce intermetallics. The interaction between the $4f$ electrons and the ligand states derived from nearest-neighbor atoms leads to a smaller volume and smaller magnetic susceptibility than implied by the valence (e.g., from x-ray absorption), as interpreted within the promotional model, these being the very trademarks of mixed-valent Ce-based systems as discussed above. An alternate point of view, which addresses the same trademarks, is the collapsed Kondo-lattice model of Allen and Martin,[10] in which it is argued that the energy required to collapse the lattice in α-Ce is available as an increase in the condensation energy of the Kondo ground state.

Valence-band photoemission experiments[11] have revealed a dramatic increase in the transition metal (TM)-derived density of states (DOS) just below E_f (the expected position of the bare $4f$ level) in going from $\rm CePd_3$ to $\rm CeRh_3$. Correspondingly, one expects a concomitant increase in the relative importance of the Fujimori channel $4f^0 \leftrightarrow 4f^1L^{-1}$, where L^{-1} is a TM-derived d-ligand hole, compared with the promotional model mixing term $4f^0(5d6s)^n \leftrightarrow 4f^1(5d6s)^{n-1}$. Since the former mixing term favors the f^1 component in the ground state, this could, in principle, explain the saturation of valence observed in the present study. The abruptness of the saturation with increasing Rh concentration may result from the hilliness of the TM-derived d band as seen in Fig. 1 of Ref. 11. We emphasize that the above discussion is offered merely as food for thought: Definitive claims must await further calculations and an experimental study of the evolution of the Tm-derived DOS near E_F in $\rm Ce(Pd_{1-x}Rh_x)_3$ in the concentration region of interest.

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