

## Photoemission study of the Ce/Rh(100) overlayer system: Hybridization of $f$ and $d$ states

C. Berg, S. Raaen, A. Borg, and H. J. Venvik

*Institutt for Fysikk, Universitetet i Trondheim, NTH, N-7034 Trondheim, Norway*

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Resonant-valence-band as well as core-level-photoemission measurements have been performed for depositions of Ce ( $\sim 0.6$ – $14$  Å) onto a Rh(100) substrate. The core-level spectra indicate formation of a mixed interface as Ce is deposited on Rh. The Rh  $3d$  core-level emission could be deconvolved into three components, which are assigned to bulk Rh, surface Rh, and rhodium that has reacted with cerium. The Ce  $4f$  emission intensity at the Fermi level is observed to move away from the Fermi level with increased Ce deposition in the submonolayer regime. The  $f$ - $d$  hybridization is argued to increase with increasing amounts of Ce in the low-coverage regime. The present findings seem to favor the picture of bandlike behavior of strongly hybridized  $f$  electrons.

### I. INTRODUCTION

Recent photoemission experiments have shown that Ce and other rare-earth atoms have a tendency to form intermixed interfaces when deposited onto various metallic substrates at room temperature.<sup>1,2</sup> The local coordination of a Ce ion may, therefore, change substantially during the initial deposition of Ce onto a substrate. The strong dependence of the photoemission on local environment in Ce systems is thus ideally suited to study the growth of an interface. The  $4f$  photoemission from Ce and its compounds has been a subject of controversy for more than one decade. Whereas the  $4f$  emission from compounds based on the heavier mixed-valent rare-earth atoms may be adequately described by the promotional model of mixed valence,<sup>3</sup> this is not the case for Ce. This is caused by strong hybridization due to spatial proximity of  $4f$  and conduction states in Ce systems. Several models have been forwarded that address this issue,<sup>4–9</sup> but none of these have yet been generally accepted to completely account for all the experimental observations.<sup>10</sup>

In this paper, we address the subjects of interface growth and strongly hybridized Ce systems by presenting a study of small amounts of deposited Ce on a Rh(100) crystal. Rhodium was chosen as the substrate material since CeRh<sub>3</sub> is the strongest mixed-valent Ce binary-intermetallic compound,<sup>3,11</sup> and thus the hybridization between  $f$  and  $d$  states is expected to be strong in the selected overlayer system. Recent x-ray-photoelectron-spectroscopy (XPS) studies of the Ce/Rh overlayer system have shown that the degree of mixed valence increases with increasing amounts of deposited Ce. The strength of the  $f$ - $d$  hybridization, as measured by the intensity of the  $4f^2$ -shakedown satellite, also shows an increase with increasing Ce amounts.<sup>12</sup> These observations may be qualitatively understood in terms of the way the Ce-Rh interface evolves.

### II. EXPERIMENT

The present photoemission experiment was performed at Beamline 22 at MAX-lab at Lund University, Sweden.

Using a modified Zeiss SX700 plane-grating monochromator in conjunction with a large hemispherical electron-energy analyzer,<sup>13</sup> a total experimental resolution of about 150 and 250 meV was obtained at a photon energy of 120 eV (resonant  $4f$  emission) and 370 eV (Rh  $3d$  core-level emission), respectively. The Rh(100) crystal was cleaned by ion bombardment, followed by cycles of heating in an oxygen atmosphere ( $p \sim 5 \times 10^{-8}$  torr) to remove carbon, and annealing in vacuum. A sharp low-energy electron-diffraction (LEED) pattern was observed after cleaning. Ce was evaporated from a resistively heated tungsten basket, which was thoroughly outgassed. The base pressure in the vacuum chamber was  $\sim 5 \times 10^{-11}$  torr, and Ce was evaporated in the  $10^{-10}$ -torr range. LEED measurements were performed, but no change in surface structure occurred for low Ce depositions,  $\lesssim 3$  Å. The diffraction spots got weaker with increased Ce deposition,  $\gtrsim 3$  Å, which shows that the interface eventually becomes disordered. The Ce deposition rate was checked before and after the experiment to verify that it remained constant. The Ce evaporation rate was estimated at  $0.3 \pm 0.2$  Å/min. The cleanliness of the sample was verified by monitoring O  $1s$  and C  $1s$  core-level emission, as well as O  $2p$  and C  $2s$  emission in the valence-band region. Oxygen and carbon could not be detected for the low Ce depositions (2, 4, or 6 min). However, traces of oxygen and carbon contamination could be seen for heavier Ce depositions (15 and 45 min). All depositions and measurements were performed at ambient temperatures.

### III. RESULTS AND DISCUSSION

The growth of the Ce-Rh interface may be envisioned as follows. Initially, for depositions of Ce considerably less than one monolayer, Ce stays on top of the substrate. This is in accordance with the lower-surface free energy of Ce as compared to Rh.<sup>14</sup> As the number of Ce atoms becomes larger, and the distance between Ce atoms becomes smaller, formation of a mixed interface occurs, in which  $f$ - $d$  hybridization is increased. This occurs since it seems to be more favorable in this situation to form Ce-

Rh bonds than to form Ce-Ce bonds. It is known that the  $f$ - $d$  hybridization is stronger for the Rh-rich compound  $\text{CeRh}_3$  than for less Rh-rich compounds, and thus the  $f$ - $d$  hybridization will be expected to increase the mixed interface evolves (i.e., as Ce acquires a larger Rh coordination), as indeed is observed from the core-level XPS measurements.<sup>12</sup>

Figure 1 shows how the Rh  $3d$  core-level photoelectron spectra varies with increasing Ce coverage. The bottom curve corresponds to the clean Rh(100) substrate. Two components, surface and bulk emission, are clearly resolved in the Rh  $3d_{5/2}$  peak near 308-eV binding energy. The low-binding-energy feature is identified as the surface component. The surface-to-bulk core-level shift was previously determined to be 0.62 eV.<sup>15</sup> When Ce is deposited onto the Rh substrate, the surface component disappears rather rapidly. Curves *b* and *c* of Fig. 1 show effective Ce depositions of  $\sim 1.5$  and  $\sim 14$  Å, respectively. After evaporation of  $\sim 14$ -Å Ce, a shift of  $\sim 0.3$  eV to lower binding energy of the bulk Rh emission is observed, and is indicative of a solid-state reaction between Ce and Rh. No change in surface structure could be detected by LEED, only a gradual weakening of the diffraction spots were observed for increased Ce depositions above  $\sim 3$  Å.

The evolution of the Rh  $3d_{5/2}$  peak with Ce deposition is shown in detail in Fig. 2. Spectra *a*, *b*, *c*, and *d* correspond to effective Ce depositions of  $\sim 0$ , 0.6, 1.8, and 1.4 Å, respectively. Three components were used to fit the data: The high-binding-energy component (dashed line) corresponds to bulk Rh, the middle component (dotted

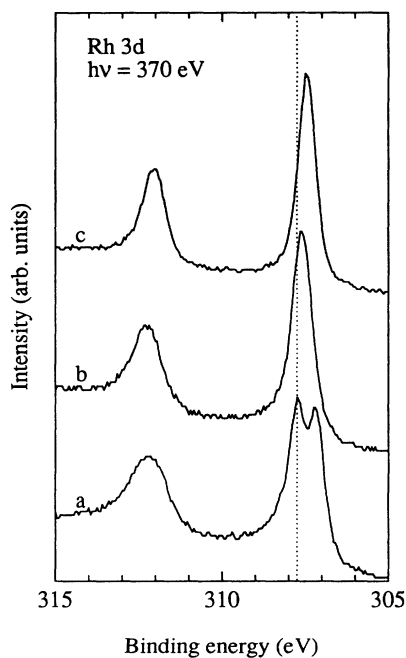


FIG. 1. Photoemission spectra from the Rh  $3d$  core-level region for various Ce depositions, recorded at a photon energy of 370 eV. The evaporation rate was estimated at  $\sim 0.3$  Å/min. Graph *a* shows the clean Rh(100) surface. Graph *b* shows the Rh  $3d$  emission after evaporating Ce for 5 min. Graph *c* is recorded after 45 min of Ce evaporation. The dotted line marks the position of the bulk  $3d_{5/2}$  emission on the bare Rh substrate.

line) corresponds to Rh, which has reacted with Ce, and the low-binding-energy peak (dot-dashed line) is interpreted to stem from surface Rh atoms. The trend is a development from a bulk and a surface component in the spectrum from pure Rh, to a situation with only one component after an evaporation of  $\sim 14$ -Å Ce. The fitting function was a convolution of a Doniach-Šunjić<sup>16</sup> and a Gaussian function, together with a linear background. The obtained fits are not unique since small variations on the fitting parameters may give visually equally good fits. However, our procedure results, presumably, in a physically reasonable deconvolution of the data.

Photoemission spectra from the valence-band region were recorded on the Fano resonance at a photon energy of 121 eV, as well as off the resonance at a photon energy of 114 eV. Results for various Ce coverages from  $\sim 0.6$  to  $\sim 14$  Å, are shown in Fig. 3. The on-resonance spectra show mainly  $4f$  emission, whereas in the off-resonance spectra  $4f$  emission is suppressed, and mainly emission from states of  $d$  symmetry occurs.<sup>17</sup> The bottom curve, Fig. 3, shows a large peak near the Fermi level. This peak is reduced while intensity is shifted to higher binding energy for increased exposures. For the largest exposures, 15 and 45 min, a peak that emerges near a binding energy of 1.3 eV predominates. For these largest Ce exposures, a Ce layer on top of the mixed Ce-Rh interface is likely to form, and part of the  $4f$  emission will be from Ce atoms that are not Rh coordinated. The data that were obtained for the two heaviest Ce exposures are less

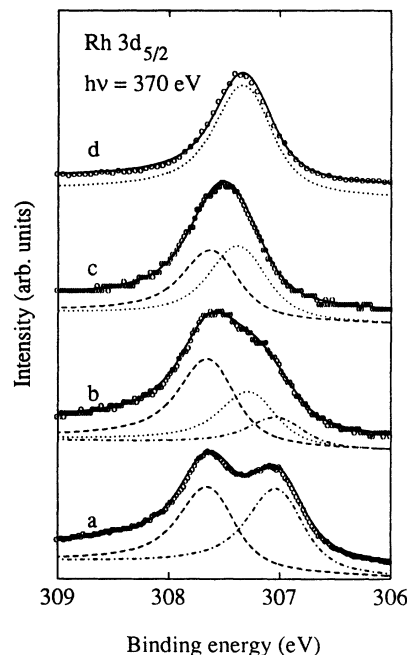


FIG. 2. Decomposition of the Rh  $3d_{5/2}$  core-level spectra for various Ce depositions. All spectra were recorded at photon energy of 370 eV. Graphs *a*, *b*, *c*, and *d* are recorded after 0, 2, 6, and 45 min of Ce evaporation, respectively. The evaporation rate is  $\sim 0.3$  Å/min. The solid lines show the overall fits to the data. The dashed lines are the bulk Rh emission, the dot-dashed lines show surface Rh emission, and the dotted lines represent emission from Rh atoms that have reacted with Ce.

useful due to a large disorder as well as to the presence of traces of carbon and oxygen contamination.

The structure of the region near the Fermi level is shown in more detail in the low Ce-coverage regime ( $\sim 0.6\text{--}1.8\text{ \AA}$ ) in Fig. 4. Two peaks, located at  $\sim 0.1\text{-eV}$  and  $\sim 0.3\text{-eV}$  binding energies, are evident in the  $4f$  emission, and the intensity is shifted from the  $\sim 0.1\text{-eV}$  peak to the  $\sim 0.3\text{-eV}$  peak as Ce is deposited on the Rh(100) substrate. The separation between the two peaks, about  $0.2\text{ eV}$ , which are spin-orbit-split components of the  $4f$  peak near the Fermi level, agrees fairly well with previous observations.<sup>9</sup> It is clear that presence of oxygen contamination will tend to reduce the  $4f$  intensity near the Fermi level, however, we feel confident that our observations were not caused by minute amounts of contamination, since neither O or C were detected for the spectra in Fig. 4.

It should be noted here that the binding energies in the present work have not been accurately calibrated. Since the position of the features near the Fermi level have been accurately determined in the high-resolution measurements of Weschke *et al.*<sup>9</sup> for CeRh<sub>3</sub>, our binding energies should, presumably, be corrected to give similar binding energies for the  $4f$  features.

The recent work of Weschke *et al.*<sup>9</sup> has demonstrated the bandlike character of the  $4f$  electrons in strongly hybridized Ce compounds by studying CeRh<sub>3</sub> at different temperatures. They find a reduction of intensity in the feature near the Fermi level as compared to the  $\sim 2\text{-eV}$  feature for reduced temperatures (increased hybridization). They also show that the relative weight next to the

Fermi level does not increase with hybridization by comparing CeRh<sub>3</sub> (strong  $f\text{-}d$  hybridization) and  $\alpha\text{-Ce}$  (weaker hybridization).<sup>9</sup> Our present observations of transfer of weight away from the Fermi level with increased Ce depositions, Fig. 4, are consistent with the findings of Weschke *et al.*<sup>9</sup> and the picture of bandlike  $4f$  electrons in strongly hybridized Ce systems, provided the  $f\text{-}d$  hybridization increases with increasing amounts of Ce deposited on Rh in the low-coverage regime, as we have argued. In addition, the work of Weschke *et al.*<sup>9</sup> shows that our observations cannot be explained by a transition from surface to bulk Ce atoms as more Ce is evaporated.

Two different descriptions based on the single-impurity Anderson Hamiltonian include the effects of the Coulomb interactions in addition to  $f\text{-}d$  hybridization, namely, the Kondo-resonance picture,<sup>4</sup> which incorporates the interaction  $U_{ff}$  between the  $f$  electrons and the screening picture,<sup>5,6</sup> which includes the interaction  $U_{fd}$  between the  $f$  and  $d$  electrons. It should be noted that the shift in  $4f$  emission intensity away from the Fermi level may be explained in the framework of the Kondo-resonance picture,<sup>4</sup> in which a transition from a  $\alpha$ -like to a  $\gamma$ -like Ce state results in a reduced intensity near the Fermi level. In this case, a decrease in the hybridization strength between  $d$  and  $f$  electrons with increased Ce deposition, contrary to what we have argued in this paper, would have to be invoked. It seems, at present, to be unclear what predictions the screening picture<sup>5,6</sup> would give as regards the dependence of the  $4f$  intensity on hybridization.

Furthermore, the structure of the on-resonance spectra

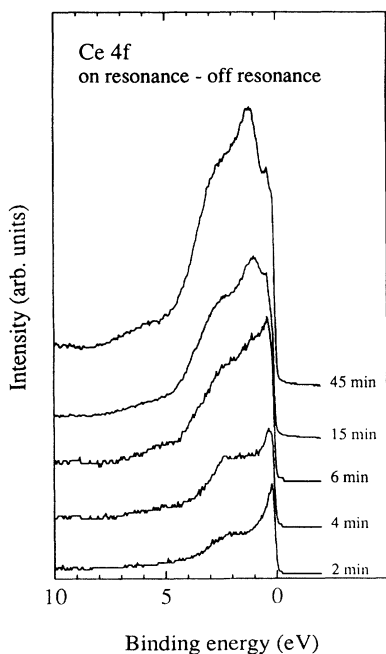


FIG. 3. Photoemission spectra from the valence-band region for various Ce depositions on Rh(100). The evaporation rate is  $\sim 0.3\text{ \AA}/\text{min}$ . The on-resonance spectra were recorded at the giant Fano resonance energy of  $121\text{ eV}$ . Off-resonance spectra ( $h\nu=114\text{ eV}$ ) have been scaled and subtracted from the on-resonance spectra.

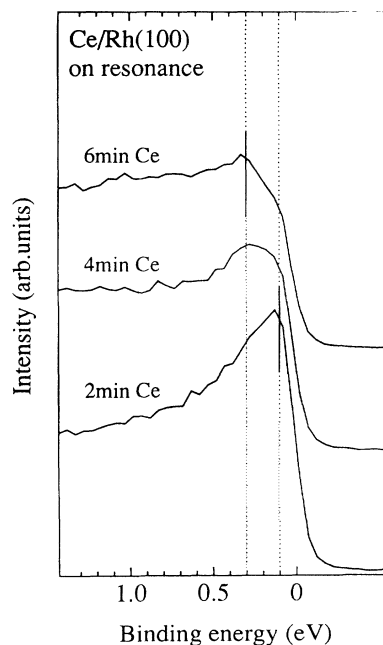


FIG. 4. The spectra are blowups in the region of the Fermi level of the low Ce coverage on-resonance spectra in Fig. 3. The positions of two features near the Fermi level are indicated by lines. Intensity is observed to shift away from the Fermi level with increasing Ce deposition.

for strongly hybridized Ce systems is expected to be even more complicated since states of  $d$  symmetry may also resonate due to strong coupling to  $f$  states. Strong  $5d$  resonance has previously been reported in various Ce compounds by Lawrence *et al.*<sup>18</sup> Evidence for a similar resonance effect was also seen on  $3d$  transition metals, where the  $2p$  levels of adsorbed oxygen were observed to resonate with the transition-metal valence bands near the  $3p$ - $3d$  excitation threshold.<sup>19</sup> Therefore, the standard procedure of subtracting off-resonance spectra from on-resonance spectra may not result in the bare  $4f$  emission in systems with strong  $f$ - $d$  hybridization.

Even though there is a tendency of increased Ce  $4f$  intensity near the Fermi level for mixed-valent Ce systems as compared to trivalent Ce systems, it is virtually impossible to deduce the degree of mixed valence based on the valence-band photoemission in Ce systems, due to the complexity of the emission in the valence-band region. By using Ce  $3d$  photoemission (in which no controversy exists), the degree of mixed valence can be deduced by measuring the intensity of the  $4f^0$  peak, and the  $f$ - $d$  hybridization can be estimated from the intensity of the  $4f^2$  peak. It should also be noted that the controversy regarding  $4f$  emission from Ce systems is not limited to strongly hybridized systems,<sup>10</sup> which have been emphasized in this paper.

#### IV. CONCLUSIONS

Shifts in the Rh  $3d$  core levels indicate formation of a mixed interface when Ce is deposited onto a Rh(100) substrate at ambient temperature. We have observed that the  $4f$  photoemission intensity is transferred away from the Fermi level as Ce is deposited in the low Ce-coverage regime. The strength of the  $f$ - $d$  hybridization is argued to increase with increased Ce deposition, as the Ce ions acquire an increased Rh coordination during the formation of the mixed interface. The present observations seem to be in accordance with the description of Weschke *et al.*<sup>9</sup> of a bandlike nature of the  $4f$  electrons in strongly hybridized Ce systems. It seems that a universally accepted many-body description of  $4f$  photoemission spectra from strongly hybridized Ce systems does not exist at this time.

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