Surface Electronic Structure of α-Like Ce Compounds

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Photoemission studies with varying degrees of surface sensitivity are reported for the Ce-$3d$ core-level and Ce-$4f$ valence-band regions of the α-like Ce compounds $CeIr_2$, $CePd_3$, and $CeRh_3$. In all cases studied, strong changes of the $4f$ electronic structure at the surface towards a more localized γ-like behavior are observed, requiring a reanalysis of previously reported photoemission spectra of α-like Ce compounds. Implications for an improved understanding of the surface-catalytic properties of Ce systems as well as of the surface electronic structure of narrow-band materials are pointed out.

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Surface valence transitions in systems of the heavy rare-earth (RE) elements Sm, Eu, Tm, and Yb are by now well understood—more than ten years after their first observation.[1-3] They are intimately related to a lowering of core-level energies at the surface of RE compounds, the so-called surface core-level shift (SCS).[2,4,5] Lowering of an unoccupied $4f$ state below E_F leads to a stabilization of a $4f$ configuration with higher occupancy at the surface, i.e., to a surface valence transition. Such valence transitions have been observed for a number of trivalent and, in particular, homogeneously mixed-valent compounds of heavy RE elements.[3,6]

Analogous surface effects have not been reported up to now for α-like Ce compounds, which are also mixed-valent systems in a qualitative sense, but with a more delocalized character of the $4f$ states than in heavy RE's.[7] The electronic structure of Ce compounds has been studied extensively in the past by various experimental methods, in particular, $3d$ core-level x-ray photoelectron spectroscopy[7,8] (XPS) and $4d \rightarrow 4f$ resonant photoemission (PE) in the valence-band region,[9] both of which are—to a varying extent—surface-sensitive techniques. The role of surface effects is therefore expected to be crucial for a correct interpretation of the results in terms of the many-body character of these systems.[10] Besides changes in stoichiometry at the surface,[11] the only surface effects reported so far are SCS's in the $4f$ spectra of some Ce systems, estimated to be smaller than 0.3 eV.[12] A bare-surface change of the electronic structure of a Ce system—though theoretically discussed[13]—has not been verified experimentally so far.

In the present Letter we report on the first unambiguous observation of surface effects on the electronic structure of Ce compounds. Applying XPS with variable photon energy ($1100\ \text{eV} \leq h\nu \leq 1700\ \text{eV}$) to the deep Ce-$3d$ core levels and resonant PE in the $4d \rightarrow 4f$ ($h\nu \simeq 122$ eV) and $3d \rightarrow 4f$ ($h\nu \simeq 882.8$ eV) threshold regions to the shallow Ce-$4f$ levels, the surface sensitivity of our measurements could be varied over a wide range. In this way, a much more localized $4f$ electronic structure was found for the outermost surface layers of the studied α-like Ce compounds as compared to the bulk, leading then to increased α-like bulk $4f$ hybridization parameters as compared to previous analyses. In the cases of $CeIr_2$ and $CePd_3$, analysis of the $3d$ core-level spectra reveals fairly γ-like surface layers. Unlike in heavy RE's, this surface valence change is not only driven by a lowering of the $4f$ binding energy (BE), but also by a decrease in $4f$ hybridization. The latter mechanism is expected to also be important for other narrow-band materials, in particular, $3d$-transition-metal compounds and high-T_c superconductors. In addition, these surface valence changes open up new ways for understanding the catalytic properties of Ce compounds.

The experiments were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using the KMC double-crystal monochromator equipped with beryl (1010) crystals and the SX700/II plane-grating monochromator of the Freie Universität; some spectra were also taken with Al-$K\alpha$ radiation. For the Ce-$3d$ core-level spectra, the total-system resolution varied as a function of photon energy from 1.2 eV ($h\nu = 1100$ eV) to 1.8 eV ($h\nu = 1700$ eV). For the Ce-$4f$ spectra, a resolution of 0.3 eV ($h\nu = 122$ eV) and 0.7 eV ($h\nu = 883$ eV) was achieved. In all experiments, PE spectra were recorded with a VG-CLAM electron spectrometer on samples cleaned *in situ* by repeated scrapping with a diamond file (base pressure in the experimental chamber, 1×10^{-10} mbar). On the basis of O-$1s$ PE at $h\nu = 900$ eV and particularly O-$2p$ PE at $h\nu = 112$ eV, an upper limit of 0.03 monolayer for possible oxygen contamination of the studied surfaces is found, which is negligible in the context of the present paper. The Ce compounds were prepared by arc melting in purified Ar atmosphere and characterized by powder x-ray diffraction.

Changes in the electronic structure at the surface of Ce compounds are expected to show up in both core-level and valence-band spectra, if taken with varying surface sensitivity. The $3d$ core-level PE spectra of $CeIr_2$ recorded for almost normal emission ($\theta = 20°$) and three different photon energies are presented in Fig. 1(a). As

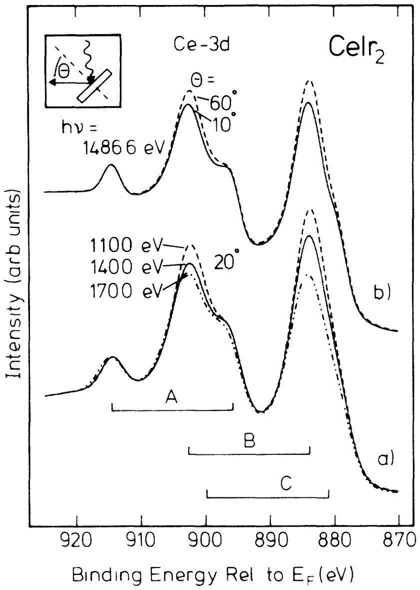

FIG. 1. Ce-$3d$ core-level PE spectra of CeIr$_2$ recorded with varying surface sensitivity: (a) for different photon energies and constant electron-emission angle, $\theta = 20°$; (b) for different angles θ and constant $h\nu = 1486.6$ eV. The spectra consist of three $3d_{3/2}$-$3d_{5/2}$ doublets due to different $4f$ final-state configurations; they are normalized to the same intensity of doublet A and corrected for background.

characteristic for α-like materials, these spectra consist of three $3d_{3/2}$-$3d_{5/2}$ spin-orbit-split doublets (A, B, and C) representing different $4f$ configurations in the PE final state and arising from $4f$ hybridization in both the initial and the final states.[10] While doublet A at the highest binding energy represents essentially a $3d^9 4f^0$ final state, the two other doublets (B and C) consist of a mixture of both $3d^9 4f^1$ and $3d^9 4f^2$ configurations, depending on the $4f$ hybridization strength. The spectra in Fig. 1(a), normalized to the same height of doublet A and corrected for inelastic background, show a clear change of the electronic structure at the surface. Taking into account the known decrease in the electron mean free path with decreasing electron kinetic energy (i.e., decreasing photon energy), the spectrum with the highest surface contribution (for $h\nu = 1100$ eV) contains a strongly increased relative intensity of doublet B, which is essentially made up of a $3d^9 4f^1$ final state. This means that the electronic structure of CeIr$_2$ at the surface is fairly γ-like, characterized by a weakly hybridized $4f^1$ ground state.

Analogous conclusions must be drawn from the Ce-$3d$ PE spectra in Fig. 1(b) taken at constant photon energy, but with two different electron-emission angles, resulting also in different surface sensitivities. Again, the more surface-sensitive spectrum for $\theta = 60°$ shows a strong increase in the relative intensity of doublet B, in full agreement with the results obtained with different photon energies.

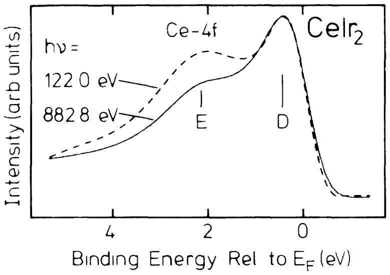

FIG. 2. Ce-$4f$ PE spectra of CeIr$_2$ in the valence-band region, obtained at the $4d \rightarrow 4f$ resonance ($h\nu = 122$ eV) and at the $3d \rightarrow 4f$ resonance ($h\nu = 882.8$ eV), respectively. The displayed 122-eV spectrum is corrected for Ir-$5d$-like valence-band contributions by subtracting the off-resonance spectrum taken at 112 eV (not shown here). Such a procedure is unnecessary in the case of the 882.8-eV spectrum, since at this photon energy the $4f$ PE cross section is about 50 times larger than that of the valence band (Ref. 14). The two spectra are normalized to equal heights of peak D and corrected for background.

The picture evolving from these Ce-$3d$ spectra is supported by $4f$ PE spectra taken in the valence-band region with different surface sensitivities (see Fig. 2). In order to suppress contributions from Ir-$5d$-like valence-band states, the strong resonance enhancement of the $4f$ photoionization cross section at the $4d \rightarrow 4f$ (at $h\nu = 122$ eV)[9] and $3d \rightarrow 4f$ (at $h\nu = 882.8$ eV)[14] core-excitation resonances of Ce is exploited. The spectra in Fig. 2 show the double-peaked structure typical for Ce compounds, with a peak D at the Fermi level and a peak E at $\simeq 2$ eV BE. This spectral shape results from the correlated $4f$ electronic structure of Ce compounds, with peak D representing mainly a $4f^1$ final state (Kondo resonance) and peak E a final state with mainly $4f^0$ configuration. The more surface-sensitive $4d \rightarrow 4f$ resonance spectrum shows an enhanced relative intensity of peak E, supporting the presence of a more γ-like surface layer in case of CeIr$_2$.

In principle, the observed surface changes in the PE spectra of CeIr$_2$ could also be caused by two other effects: (i) the presence of trivalent cerium oxide at the surface and (ii) surface segregation of Ce giving rise to γ-like Ce islands. From O-$1s$ and O-$2p$ PE signals, oxygen contamination was found to be negligible. Ce segregation to the surface can also be ruled out on the basis of PE studies of Ce-$4d$ and Ir-$4f$ core levels with different photon energies and different electron-emission angles, i.e., with varying surface sensitivity. These studies did not give any hint of changes in stoichiometry at the surface.

For a more quantitative analysis of the PE experiments, we employed a simplified version of the Gunnarsson-Schönhammer (GS) theory proposed by Imer and Wuilloud.[15] In this model, the energy splittings and relative intensities of the three final states, labeled A, B, and C in Fig. 1, are calculated as a function of the parameters ϵ, U_{ff}, U_{fc}, and Δ. Here, ϵ stands for the energy of the unhybridized $4f^1$ state (relative to E_F), U_{ff} for the Coulomb repulsion between $4f$ electrons at the same site, U_{fc} for the Coulomb attraction between a $4f$ electron and the final-state core hole, and Δ for the effective hybridization energy between $4f$ states and the conduction band. Two sets of parameters for ϵ and Δ were used to describe bulk and surface components. The surface-to-bulk PE intensity ratios as a function of electron kinetic energy were assumed to be the same as determined experimentally for Yb metal,[16] where surface and bulk contributions to the $4f$ PE spectrum are well separated.

For kinetic energies of 200, 500, and 800 eV, surface-to-bulk ratios of 0.90, 0.63, and 0.55, respectively, were derived, in good agreement with the results of calculations for the mean free path of $\mathrm{CeIr_2}$ using the theory outlined in Ref. 17. The curve profile was composed of Lorentzian lines with different widths for the three components A, B, and C as well as for surface and bulk to account for differences in multiplet structures and lifetime broadening. Contributions from scattered secondary electrons were simulated by an integral background coupled to bulk emission as well as by a smooth parabolic function. The calculated spectrum was convoluted by a Gaussian function to account for the finite experimental resolution.

The results of least-squares fits with these curve profiles are shown in Fig. 3 for the Ce-$3d$ spectra of $\mathrm{CeIr_2}$ taken at the three specified photon energies. Consistent fits were only achieved for a strongly reduced $4f$ hybridization in the outermost surface layer on $\mathrm{CeIr_2}$, giving rise to almost a single spin-orbit-split surface $3d$ PE doublet (dotted curves in Fig. 3). Analogous analyses were performed for $\mathrm{CePd_3}$ and $\mathrm{CeRh_3}$. Table I summarizes the resulting bulk and surface fit parameters for the three α-like Ce compounds studied.

For all three compounds, larger bulk hybridization parameters Δ^b and smaller $|\epsilon^b|$ values are obtained as compared to an analysis without consideration of a surface change in the $4f$ electronic structure. In the case of $\mathrm{CeIr_2}$, these differences are $\simeq 0.2$ eV for Δ^b and $\simeq 0.5$ eV for ϵ^b, leading to a $\simeq 10\%$ smaller value of the $4f$ occupancy n_f. For the surface, Δ^s values are found to be rather small as compared to the respective bulk values, resulting in n_f values very close to 1. With an estimated uncertainty of 50% in the experimental surface-to-bulk ratios, the rather conservative error bars given in Table I are obtained.

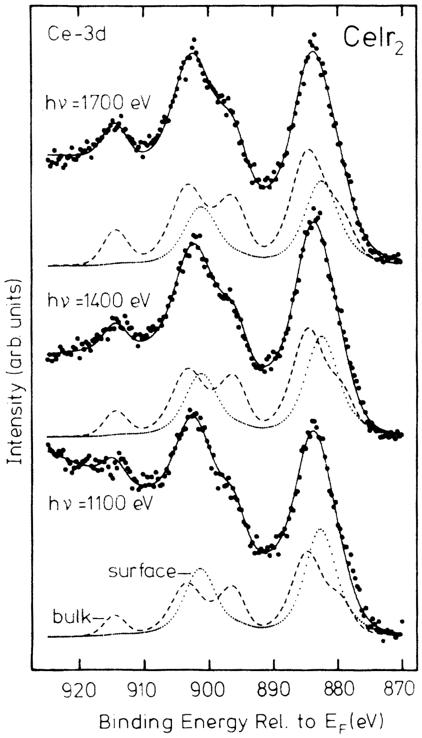

FIG. 3. Results of least-squares-fit analysis (solid curve) of the Ce-$3d$ core-level PE spectra of $\mathrm{CeIr_2}$ taken at $\theta = 20°$ and the three specified photon energies. The component spectra from surface and bulk emission are given by the dotted and dashed curves, respectively.

For $\mathrm{CeIr_2}$ and $\mathrm{CePd_3}$, the surface ϵ parameters, ϵ^s, cannot be derived unambiguously from the $3d$ PE spectra, since the dependence of the spectral shape on ϵ^s is quite weak in these cases due to the small Δ^s values. For $\mathrm{CeIr_2}$, however, we can obtain an estimate for ϵ^s from the Ce-$4f$ PE spectra presented in Fig. 2. Within the applied model, the BE of peak E depends on ϵ and Δ by the expression $(\epsilon^2+4\Delta^2)^{1/2}$, if admixtures of the $4f^2$ configuration in the ground state are neglected. Since the energy position of peak E does not change as a function of surface sensitivity, a BE of $\simeq 2$ eV is found for both bulk and surface. With $\Delta^s = 0.26$ eV, we thus obtain a value for $|\epsilon^s|$ that is $\simeq 0.8$ eV larger than the respective bulk value. For $\mathrm{CeRh_3}$, where the surface hybridization

TABLE I. Summary of fit parameters for the Ce-$3d$ PE spectra of the three compounds studied (in eV). In all cases, $U_{ff} \simeq 7$ eV and $U_{fc} \simeq 10$ eV were used for bulk and surface with small variations for the different compounds (for the entries in parentheses, see text).

	ϵ^b	ϵ^s	Δ^b	Δ^s	n_f^b	n_f^s
$\mathrm{CeIr_2}$	-0.96 ± 0.05	(-1.7)	0.88 ± 0.02	$0.26^{+0.17}_{-0.26}$	0.81 ± 0.02	(0.98)
$\mathrm{CePd_3}$	-1.14 ± 0.05	(≤ -1.8)	0.82 ± 0.02	$0.25^{+0.17}_{-0.25}$	0.85 ± 0.02	(0.99)
$\mathrm{CeRh_3}$	-1.04 ± 0.12	-2.08 ± 0.20	1.04 ± 0.03	0.52 ± 0.10	0.81 ± 0.03	0.97 ± 0.03

is not so small, we derive a similar value from the 3d PE spectra alone (see Table I). It should be emphasized here that it is this shift in ϵ that corresponds to the classical SCS observed for heavy RE compounds and not a possible experimental shift in the BE of peak E. This relation is further illustrated by our recent observation of a SCS of 0.7 eV for LuIr$_2$,[16] in close agreement with the surface shift in ϵ derived here for CeIr$_2$.

Finally, some implications of the present results are addressed: (i) The considerable work on deriving Ce-4f occupancies and GS parameters from XPS measurements of Ce compounds, in which surface effects were not considered,[7,9] will have to be reviewed. As an example, the reported discrepancy between experimental and theoretical 4f valence-band PE spectra, calculated with ϵ and Δ parameters from 3d XPS spectra,[9] is readily explained as a consequence of a surface valence change. (ii) The catalytic properties of α-like Ce compounds may well be related to the presence of an almost γ-like surface layer that has the potential of acting as an electron donor to adsorbed species. In this respect, it is interesting to note that good catalytic properties are shown particularly by those α-like intermetallic compounds which are expected—on the basis of the present results—to be fairly γ-like on the surface.[18] (iii) Surface effects on the correlated electronic structure analogous to those reported here for Ce compounds may be expected for compounds of other light RE's, of light actinides, and even of 3d transition elements, including copper-based high-T_c superconductors. This is supported by our most recent experimental results on compounds of La, which show analogous effects to those reported here.[16]

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