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Surface and bulk electronic structure of Ce metal studied by high-resolution resonant photoemission

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High-resolution resonant photoemission (PE) at the $4d \rightarrow 4f$ and $3d \rightarrow 4f$ thresholds is applied to study the electronic structure of Ce metal. Due to the different surface sensitivities, the resulting $4f$ PE spectra, which are almost free of non-$4f$ background, reflect directly a substantial change in $4f$ electronic structure of α-Ce metal towards γ-like behavior at the surface. This finding resolves a longstanding discrepancy between the results of surface-sensitive $4f$ PE and those of bulk model calculations. Pure surface and bulk $4f$ PE signals are derived for α-Ce metal.

Electronic systems at the borderline between localized and itinerant behavior are attracting considerable interest, since they reveal a number of exotic properties, such as Kondo or heavy-fermion phenomena.[1] In particular, elemental Ce metal with its isostructural γ-α phase transtion has been the subject of numerous experimental and theoretical studies.[2-5] This phase transition is intimately related with the strong interactions between the single $4f$ electron and conduction-band states. Many attempts have been made in the past to investigate the electronic structure of Ce metal by means of high-energy spectroscopies.[2-4] Due to the correlated nature of the states involved, an interpretation of the experimental spectra in terms of ground-state properties is not straightforward. Most successful in this respect has been a description of $4f$ systems by a modified Anderson single-impurity model.[6-9]

Among the various high-energy spectroscopies, photoemission (PE) from $4f$ states provides the most direct insight into ground-state properties, since the perturbations of the system are small as compared to deeper core excitations. It was shown that even low-energy excitations at the Fermi level (E_F) are accessible to direct study by high-resolution PE using He discharge lamps.[4,9] The restriction to the low He I ($h\nu$=21.2 eV) and He II ($h\nu$=40.8 eV) photon energies carries the disadvantages that (i) contributions from valence-band states are intense in the resulting spectra and (ii) the PE measurements are extremely surface sensitive. Therefore, the $4f$ signals were derived—due to (i)—by subtracting spectra taken at two different photon energies, which may not lead to a complete elimination of non-$4f$ contributions. In addition, the difference spectra—due to (ii)—are not necessarily representative of the bulk in view of the recent observation of surface effects on the electronic structure of α-like intermetallic compounds of Ce.[10] These difficulties may be avoided by resonant $4d \rightarrow 4f$ and $3d \rightarrow 4f$ PE,[2,11] where the $4f$ signal is resonantly enhanced and the PE cross sections of valence band states are low. Up to now, however, the resolution, even in $4d \rightarrow 4f$ resonant PE, was far too low for resolving $4f$ fine structures close to E_F.[2,8]

In this Brief Report we report on the first $4d \rightarrow 4f$ resonant PE study (at $h\nu \simeq 122$ eV) of γ- and α-Ce metal with a total-system resolution of 40 meV [full width at half maximum (FWHM)]. The spectrometer used enabled us to take in addition $3d \rightarrow 4f$ resonant PE spectra (at $h\nu \simeq 884$ eV) from the same samples. In this way, a substantial surface change of the electronic structure of α-Ce metal was discovered. The surface and bulk $4f$ PE signals of α-Ce metal, derived from the measured $4d \rightarrow 4f$ and $3d \rightarrow 4f$ spectra, reveal directly a γ-like character of the outermost surface layer and a far more hybridized bulk than previously assumed, when surface effects were not considered. This surface change readily offers an explanation for a longstanding discrepancy[8] between the results of surface-sensitive PE measurements and those of bulk model calculations.

The experiments were performed with a spectrometer combining the high resolving power of the SX700/II monochromator at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) with a high-resolution hemispherical electron analyzer (Leybold-Heraeus, EA-11). The SX700/II monochromator, operated by the Freie Universität Berlin, sets presently the resolution standard in the photon-energy range from $\simeq 40$ to $\simeq 900$ eV employing a single 1221-lines/mm plane grating. In first order of diffraction, linewidths (FWHM) as low as $\simeq 3$ meV at $h\nu$=40 eV, $\simeq 17$ meV at $h\nu$=120 eV, and $\simeq 300$ meV at $h\nu$=900 eV are expected.[12] To gain signal intensity, both the monochromator and the electron spectrometer (resolution presently ≥ 20 meV) were operated away from optimum performance, leading to a best total-system resolution of 40 meV (FWHM) at $h\nu$=122 eV. The studied polycrystalline films were prepared *in situ* by depositing high-purity Ce metal onto a Cu substrate cooled to 150 and 20 K, respectively, to obtain γ- and α-Ce metal. The base pressure in the experimental chamber was 7×10^{-11} mbar, rising to 1×10^{-9} mbar during deposition. This led to oxygen-free Ce films as monitored via O $2p$ PE at $h\nu$=40 eV.

Figure 1 displays high-resolution PE spectra of γ- and α-Ce metal taken in the region of the giant $4d \rightarrow 4f$ resonance. To reduce thermal broadening, γ-Ce metal was

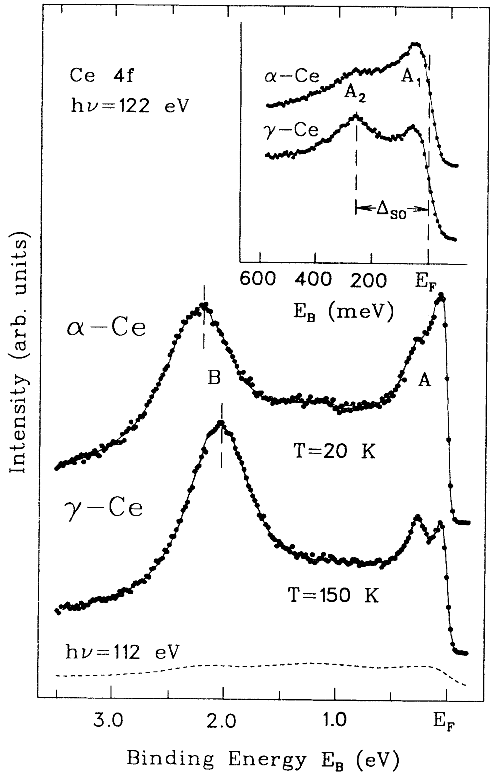

FIG. 1. High-resolution $4d \rightarrow 4f$ resonant PE spectra of γ- and α-Ce metal. The inset shows the region of peaks A_1 and A_2 on an expanded energy scale, recorded with a total-system resolution of 40 meV (FWHM). For comparison, a properly normalized off-resonance spectrum of α-Ce metal ($h\nu = 112$ eV) is included (dashed curve).

kept at 150 K, well above the γ-α phase-transition temperature, while α-Ce metal was studied at 20 K. These spectra may well represent the present resolution record in PE with soft x rays ($h\nu \geq 100$ eV). Before, similar resolutions were only achieved in PE studies using He discharge lamps.[4] Non-$4f$ contributions to the resonant PE spectra are negligible, as illustrated by the off-resonance spectrum of α-Ce metal taken at $h\nu = 112$ eV (dashed spectrum in Fig. 1).

Both spectra consist of a doublet A close to E_F and a more intense peak B at a binding energy of $\simeq 2$ eV (2.2 eV) in case of γ-Ce (α-Ce) metal. The assignment of features A and B to essentially $4f^1$ and $4f^0$ final states, respectively, is now generally accepted.[6] The inset shows the region around doublet A on an expanded energy scale with the two components A_1 and A_2 separated by $\simeq 280$ meV, reflecting the spin-orbit splitting.[4] When going from γ-Ce to α-Ce metal, peak B shifts to higher binding energy, while feature A—and in particular component A_1— gains in relative intensity. These resonant PE spectra confirm the general observations made previously for γ- and α-Ce metal in low-resolution resonant PE (Ref. 2) and in high-resolution nonresonant PE with He I and He II light.[4] In distinction to these previous studies, however, the present spectra represent highly resolved direct images of the $4f$ electronic structure virtually free of non-$4f$ background.

The spectral shape of the $4f$ PE spectrum in the valence-band region has been calculated for γ- and α-Ce metal by single-impurity Anderson-type models, with parameters derived from $3d$ x-ray core-level photoelectron spectroscopy (XPS) results.[4,9] While there is qualitative agreement with the experimental spectra, a quantitative comparison reveals discrepancies in width and spectral weight of peak B. In both cases, the model calculations simulate much larger *widths* of peak B than observed and—in the case of α-Ce—much less spectral *weight*. The discrepancy in spectral *width* may be due to an inappropriate choice of the valence-band shape (due to a critical influence on the calculated spectral shape in the region of peak B),[6,9] that cannot account for the discrepancy in spectral *weight*, however. Since $3d$ core-level XPS (electron kinetic energy $E_k \simeq 600$ eV with Al $K\alpha$ x rays) is much more bulk sensitive than $4d \rightarrow 4f$ resonant PE ($E_K \simeq 120$ eV), the latter discrepancy suggests a more γ-like surface of α-Ce metal. Similar effects were recently observed in a more indirect way for a series of α-like intermetallic compounds of Ce using Ce $3d$ core-level PE with tunable photon energy.[10] Here, we demonstrate such a surface change in the $4f$ electronic structure in a very direct way by monitoring the $4f$ states with different surface sensitivities through $4d \rightarrow 4f$ and $3d \rightarrow 4f$ resonant PE.

Figure 2 shows $4d \rightarrow 4f$ and $3d \rightarrow 4f$ resonant PE spectra of γ- and α-Ce metal taken with about equal total-system resolutions. The 884-eV spectra are much more bulk sensitive than those obtained at $h\nu = 120$ eV. For a direct comparison of these spectra, however, one has to consider that the ratio of intensities of peaks A and B varies slightly with photon energy across the resonances.[8,13] We therefore chose the photon energies in

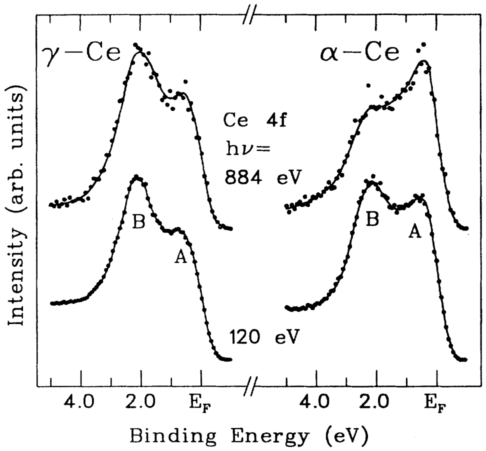

FIG. 2. Resonant PE spectra of γ- and α-Ce metal, taken at the $4d \rightarrow 4f$ ($h\nu = 120$ eV) and $3d \rightarrow 4f$ ($h\nu = 884$ eV) resonance, respectively. To facilitate a comparison, the total-system resolutions were set equal in both ($= 700$ meV, FWHM). The solid lines serve as guides to the eye.

such a way that in the surface-sensitive $4d \rightarrow 4f$ resonant PE spectra, peak A, in the $3d \rightarrow 4f$ case, peak B were most intense. This choice of photon energies actually underestimates slightly the observed surface effect, and leads to essentially no difference in the spectra of γ-Ce. In case of α-Ce, however, a drastic difference is observed, with the weight of peak B being strongly reduced in the bulk-sensitive $3d \rightarrow 4f$ spectrum. This reflects clearly the presence of a γ-like surface layer.

For a better comparison with the results of model calculations, we decomposed the two spectra into signals from the bulk and the outermost surface layer. This was achieved by a simple subtraction method, where—following Ref. 14, and in agreement with experimental data on Sm-metal—the surface-to-bulk intensity ratios were estimated as 0.8 and 0.2, respectively, for electron-kinetic energies of 120 and 884 eV. The results are presented in Fig. 3. As expected, the surface component of α-Ce metal looks almost γ-like, while the bulk component reveals a strongly reduced intensity of peak B, in agreement with the results of model calculations.

For a more quantitative description of these pure bulk and surface spectra, we used the simplified Imer-Wuilloud version[15] of the Gunnarsson-Schönhammer formalism.[6] To this end, peaks A and B were described by Lorentzians, multiplied by the Fermi distribution function, and convoluted with a Gaussian to simulate finite experimental resolution; peak A was pinned to E_F. The binding energy of peak B and the relative intensities were calculated within the model as a function of the $4f^1$ single-particle energy ϵ, the hybridization parameter Δ, and the intra-atomic Coulomb correlation energy U_{ff}. Assuming $U_{ff}=8$ eV, reasonable fits to the bulk spectrum are obtained for $\epsilon_b=-0.7$ eV and $\Delta_b=0.9$ eV, whereas the surface spectrum is described by $\epsilon_S=1.2$ eV and $\Delta_S=0.7$ eV. This confirms the trend found previously for intermetallic compounds of Ce,[10] including a reduction of Δ at the surface and—as in the case of localized $4f$ systems—a lowering of ϵ.[16] Even though the simplified model applied describes the trend qualitatively correct, one should not overvalue the magnitude of the derived parameters, since the PE spectrum is known to be influenced by the shape of the valence band neglected here.[6]

The inset in Fig. 3 displays the bulk contribution to the high-resolution $4d \rightarrow 4f$ resonant PE spectrum of α-Ce derived from the spectra in Fig. 1 (inset) in an analogous way, assuming a spectral shape of the surface contribution equal to the measured spectrum of γ-Ce. Note that peak A_2 almost disappears, relative to the dominant peak A_1 at E_F. This is a remarkable difference to the spectra of Ref. 4 and is also not reproduced by the model calculations of Refs. 4 and 9, because the magnitude of hybridization was underestimated in these calculations due to a neglect of surface effects. Note that the shape of the spectrum in the inset of Fig. 3 is not influenced by the resonance process, since the ratio of intensities of peaks A_1 and A_2 in the spectra of Fig. 1 was found not to vary with photon energy across the resonance.

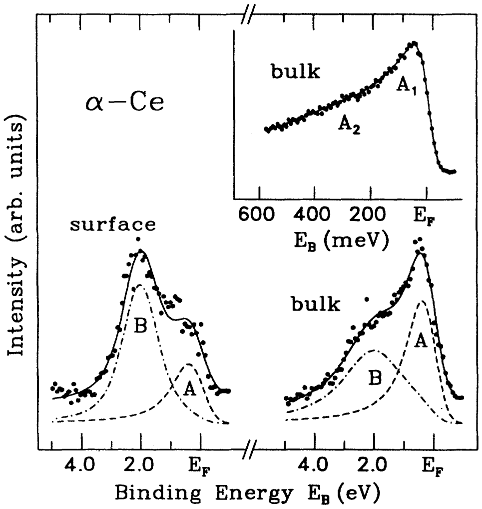

FIG. 3. Surface and bulk PE spectra of α-Ce metal derived from the spectra of Fig. 2 as described in the text. The solid lines represent the results of model calculations (see text). Note that the larger linewidth of peak B in the bulk spectrum is due to the increased hybridization (Ref. 6). The inset displays the bulk contribution to the high-resolution $4d \rightarrow 4f$ resonant PE spectrum of α-Ce metal in the region close to E_F, derived in an analogous way from the spectra in Fig. 1; the solid line serves as a guide to the eye.

In summary, we have achieved resonant $4d \rightarrow 4f$ PE with a total-system resolving power of $E/\Delta E \simeq 3.000$, and applied it to study directly the low-energy excitations in Ce systems. This opens new perspectives in investigating fine details of the $4f$ electronic structure close to E_F of strongly hybridized compounds of Ce and other rare-earth elements. In this way, even rare-earth intermetallic compounds with transition metals may be studied with meV resolution, when at off-resonance energies the $4f$ signals are masked by strong d-band emission. Furthermore, by comparing $3d \rightarrow 4f$ and $4d \rightarrow 4f$ resonant PE spectra taken from the same samples, a substantial surface change of the $4f$ electronic structure of α-Ce metal towards a γ-like behavior was discovered. This readily explains a long-standing discrepancy between experimental results and those of model calculations and demonstrates the necessity of considering surface effects in theoretical descriptions of Ce systems.

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