

The Ce 4*f* surface shift: A test for the Anderson-impurity Hamiltonian

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Evidence is provided of the role of the different hybridization strengths between the surface and the bulk in determining the magnitude of the surface shift for the shallow Ce 4*f* levels, with respect to the deeper core levels. This was achieved by comparing the photoemission core levels for a weakly hybridized case (CeAl) to a case of intermediate hybridization (γ -Ce). For CeAl a 4*f* surface shift of 0.45 eV was observed, similar to that for the 5*p* core level, whereas a smaller (if any) 4*f* surface shift was observed for γ -Ce. Model calculations based on the Anderson impurity Hamiltonian are shown to give a correct evaluation of this effect, which can be exploited as a way of testing the results of such a description for the Ce *f* states. [S0163-1829(96)50348-6]

Metallic Ce-based materials have attracted considerable attention^{1,2} since they offer a unique opportunity for studying the behavior of strongly correlated 4*f* electrons on the verge of localization. A widely used description of the Ce 4*f* electrons has been based on the $1/N$ expansion of the Anderson impurity Hamiltonian (AIH).³ In its simplest formulation the model describes the *f* electrons as impurities, isolated from each other because of the negligible direct *f*-*f* overlap. On the other hand, these *f* levels interact with the extended states of other symmetries via a hybridization term representing the hopping matrix element averaged over the valence band energy region. Recently,⁴ however, the full validity of this model has been somewhat questioned even in cases where low hybridization occurs. Therefore a comparison between the experiments and the predictions of the AIH model may give some further arguments to this important issue.

From this point of view the case of Ce 4*f* surface core level shift (SCS), as directly related to the reduced cohesive energy at the surface with respect to the bulk, is very puzzling since, despite an expected 4*f* SCS of ~ 0.5 eV (Ref. 5) in analogy with the findings on polycrystalline light *R*'s,^{6,7} experimental results^{6,8} gave no evidence for such a shift in pure Ce. Recently, however, a hybridization effect has been suggested⁹ as being responsible for this behavior.

By comparing the photoemission (PE) 4*f*-related line shapes of CeAl and γ -Ce, the role of hybridization in determining the total magnitude of the Ce 4*f* surface shift is definitely clarified and therefore exploited to test the predictions of the AIH model: a nice agreement with the experiments is found herein, indicating the ability of the model to correctly account for the "hybridization" shift of the Ce 4*f* ionization feature.

Homogeneous polycrystalline CeAl was prepared by induction melting from stoichiometric amounts. The quality was checked by x-ray diffraction and microprobe analysis.

Pure (99.9%) Ce lump was used as γ -Ce. PE measurements were performed on beamline 22 at MAX-Lab¹⁰ in normal emission geometry. An overall energy resolution between 0.06 and 0.8 eV (full width at half maximum) was achieved in the 100–900 eV $h\nu$ range. The samples were cleaned by scraping with a diamond file in vacuum (base pressure 7×10^{-11} mbar). Sample cleanliness was checked with the O 1*s*, C 1*s*, and O 2*p* signals. The surface stoichiometry of CeAl was determined by use of the core level peak intensities and was found to be in excellent agreement with the bulk stoichiometry. Careful calibration of the energy scale was obtained by means of the Fermi edge and the 4*f* core levels of a clean gold reference.

In order to disentangle the surface from the bulk Ce 4*f* contributions, PE measurements with different surface sensitivities are needed. Furthermore, due to the low Ce 4*f* occupation in the ground state (close to one), the 4*f* spectral weight is generally smaller than that of the other valence orbitals and a resonance enhancement effect has to be exploited to get reliable 4*f* line shapes.¹ These two requirements may be fulfilled by resonant PE (RPE) at the Ce 4*d* and Ce 3*d* thresholds ($h\nu \sim 120$ eV and ~ 880 eV, respectively)^{8,11} via an intermediate $d \rightarrow 4f$ absorption process. In fact, the difference in the kinetic energies of the 4*f* photoelectrons corresponding to the two thresholds results in a significant variation of the escape depth: the 4*d* \rightarrow 4*f* RPE spectra have a larger surface sensitivity as compared to the 3*d* \rightarrow 4*f* RPE spectra, which are more sensitive to the bulk. As thoroughly discussed in the literature,^{1,8,11,12} in both cases the non-*f* contributions to the valence band spectra may be eliminated by subtracting the off-resonance spectra from the on-resonance ones.

In Fig. 1 the results of such a subtraction procedure are shown for CeAl and γ -Ce representing the 4*f*-related spectral intensities at the Ce 4*d* (black dots) and Ce 3*d* (open dots) thresholds. For a direct comparison between the spec-

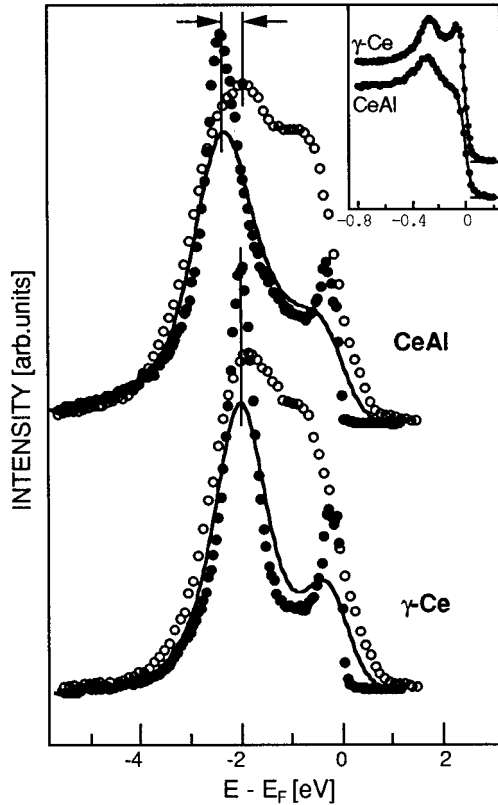


FIG. 1. Ce 4*f* line shapes of CeAl and γ -Ce obtained at the Ce 4*d* (black dots) and Ce 3*d* (open dots) thresholds. The 4*f* line shapes at the Ce 4*d* threshold are also shown (lines) after a Gaussian broadening with a 0.8 eV FWHM accounting for the different resolutions, in order to be directly comparable to the spectra at the Ce 3*d* threshold. As indicated by arrows, in CeAl the maxima by the f^0 intensity in the two spectra are shifted by ~ 0.5 eV. The inset shows the f^1 fine structure as measured at the 4*d* resonance ($h\nu=122$ eV).

tra, the 4*f* line shapes at the Ce 4*d* thresholds are also shown (lines) after a Gaussian broadening accounting for the different experimental resolutions. In all cases, two features are clearly seen in the spectra which are assigned to the f^1 emission, close to the Fermi energy (E_F), and to the f^0 emission at ~ 2 eV below E_F .^{1,3} The trend shown by the f^1/f^0 intensity ratio agrees with the expectations: at the Ce 4*d* threshold the larger surface sensitivity results in a less pronounced f^1 intensity indicating a reduced surface hybridization with respect to the bulk.^{8,9,11} By a closer inspection of the f^0 feature it is clear, already at this stage, that while no clear shift can be detected in γ -Ce by varying the surface sensitivity, a shift as large as ~ 0.5 eV is present in CeAl (shown in Fig. 1 by arrows). This result is, to our knowledge, the first experimental evidence for a Ce 4*f* surface shift.

In order to understand the difference between γ -Ce and CeAl, we have also performed surface sensitive Ce 5*p*_{3/2} core-level PE at various $h\nu$ (40–200 eV range). In fact, for R^3 's it is known^{5,7} that the magnitude of the SCS is not dependent upon the shell. Ce 5*p* SCS's of 0.6 and 0.5 eV have been found for CeAl and γ -Ce, respectively, with the surface peak at higher binding energy. While the value obtained for

CeAl is close to the Ce 4*f* surface shift shown in Fig. 1, the magnitude of the 5*p* and 4*f* surface shifts is considerably different for γ -Ce. Some other effect has therefore to be taken into account to reconcile these different behaviors.

In the AIH description of the Ce 4*f* states the effect of hybridization results in a decrease of the total energy and a shift of the 4*f* levels to larger binding energy. The hybridization strength critically depends upon the local coordination of the Ce atoms and is known^{8,9} to significantly decrease at the surface with respect to the bulk, as mentioned above. This may therefore cause a variation of the total 4*f* surface shift (herein just "surface shift") with respect to the SCS. In the limit of extremely small hybridization a Ce 4*f* surface shift with a magnitude similar to the SCS measured on the inner 5*p* shell may be expected. On the other hand, if a larger reduction in the 4*f* hybridization takes place on going from the bulk to the surface, a larger reduction of the observed 4*f* surface shift may occur, with respect to the magnitude of the 5*p* SCS. At variance with the case of deep core levels, where usual SCS's occur, the PE results for the Ce 4*f* states should therefore be interpreted in terms of two opposite and competing mechanisms which tend to cancel out.

The two systems investigated display different strengths of the 4*f* hybridization with the continuum states and have indeed been chosen for this particular reason. This is directly reflected in the measurements. High resolution spectra of the f^1 fine structure (Fig. 1, inset) show that two clear features may be distinguished: a spin-orbit sideband around 280 meV and a sharp leading edge structure at E_F due to the combination of the crystal field sideband and the tail of the so-called Kondo resonance (KR). It has recently been shown^{13,14} that the intensity ratio between these two features scales with the Kondo temperature, T_K (i.e., with the hybridization strength) giving a more intense KR for larger T_K . The inset of Fig. 1 shows therefore that the hybridization strength is considerably larger in γ -Ce than in CeAl, in analogy with estimation of the bulk T_K 's which are ~ 100 K (Ref. 9) and ~ 20 K,¹⁵ respectively. We speculate that this difference between γ -Ce and CeAl is responsible for the above discrepancy between the experimental surface shifts for the Ce 4*f* and 5*p* levels. In fact, the SCS represents the difference between the surface and bulk *unhybridized* f^0 energies ($\varepsilon_f^{\text{surface}}$ and $\varepsilon_f^{\text{bulk}}$, respectively), while the experimental f^0 peaks lie at larger binding energies due to extra (hybridization) shifts. In case of γ -Ce the remarkable variation of the hybridization strength between surface and bulk [surface $T_K \sim 25$ K (Ref. 9)] shifts the bulk f^0 peak toward the surface f^0 peak, whose hybridization shift is instead considerably smaller. This results in a strongly reduced (if any) surface shift. On the other hand, in CeAl the surface and bulk f^0 hybridization shifts are both small, because of the low T_K , resulting in a 4*f* surface shift similar, though slightly smaller as expected, to the Ce 5*p* SCS. We note that a somewhat similar behavior, though considerably smaller in magnitude, is shown by the f^2 addition peak above E_F as shown by inverse photoemission spectroscopy.¹⁶

A 4*f* line-shape analysis is presented in Fig. 2 for CeAl. The 4*f* spectral functions at the two thresholds are decomposed into three different contributions each, with unchanged position and shape (apart from the Gaussian broadening): (i) the f^1 feature with its spin-orbit component, which is a mix-

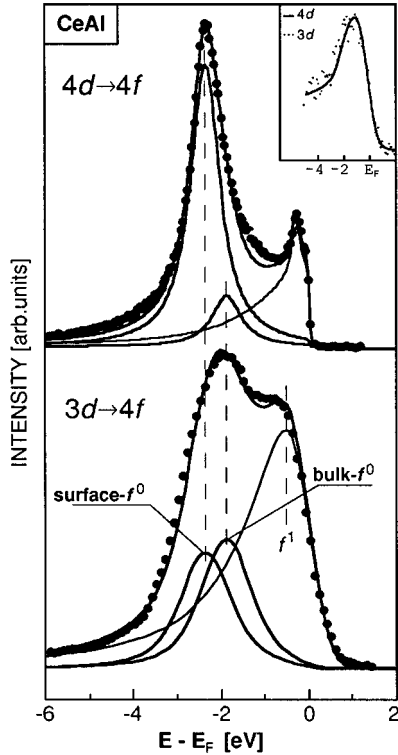


FIG. 2. Ce 4f spectral function of CeAl (dots) extracted at Ce 4d and Ce 3d thresholds. Both curves are decomposed into one f^1 and two f^0 components with the same Lorentzian shape (a bulk f^0 peak at 1.90 eV and a surface f^0 peak at 2.35 eV below E_F) as explained in the text. A Gaussian broadening (with FWHM=0.06 eV and 0.8 eV for the 4d and 3d thresholds, respectively) has been added to all components to account for the experimental resolution. The sums of these three components are also shown as solid lines. Inset: off-resonance valence band spectra at the Ce 3d ($h\nu=875$ eV, dots) and 4d ($h\nu=114$ eV, line) thresholds, after a Gaussian broadening of the latter to simulate the same experimental resolution.

ture of bulk and surface emissions; (ii) the (Lorentzian) bulk f^0 peak at 1.9 eV; (iii) the surface f^0 peak, with identical shape to (ii), at 2.35 eV. We stress that, even by leaving some degree of freedom to the overall f^1 line shape, which is not known *a priori*, reasonable decompositions of both the 4f spectra were only achievable by using two f^0 components separated by 450 ± 50 meV. Taking into account the estimates of the escape depths (λ) for the measurements in Fig. 2 [$\lambda_{4d} \sim 4.5$ Å, $\lambda_{3d} \sim 15$ Å (Ref. 17)] the scaling of the $f_{\text{surface}}^0/f_{\text{bulk}}^0$ intensity ratio vs $h\nu$ gives a surface depth of 5 Å for CeAl, which corresponds to about two monolayers. This result is in good agreement with estimations made with different spectroscopies^{11,18} on other polycrystalline *R* compounds, thus giving further confidence to the present analysis. A similar decomposition made on γ -Ce *does not* unambiguously provide evidence for two shifted f^0 components and gives an upper limit of 0.2 eV to the 4f surface shift.

In order to apply the AIH model to our results, we have determined the surface- and bulk-related 4f spectral functions for CeAl (shown in Fig. 3), exploiting RPE results at the Ce 4d and 3d thresholds¹⁹ as described in Refs. 8 and 11.

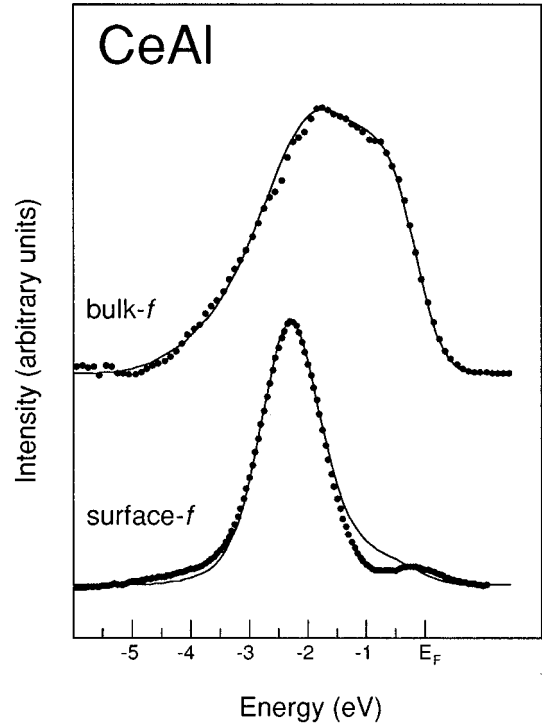


FIG. 3. Experimental (dots) and theoretical (lines) surface and bulk f spectral functions for CeAl. See text for details.

The present calculation of the f spectral functions have been performed using different ε_f and hybridization strengths for the surface and the bulk. As mentioned above, they describe the interaction between an f impurity, at energy ε_f with a finite on-site Coulomb interaction (U_{ff}), and an extended semielliptical model band crossing E_F , showing that by increasing the f^1/f^0 intensity ratio a progressive f^0 hybridization shift takes place. In case of CeAl the comparison between theory (lines) and experiments (dots) is shown in Fig. 3 for both bulk- and surface- f spectral functions: the model gives an f^0 hybridization shift of ~ 0.1 eV and ~ 0.25 eV for surface and bulk, respectively. Hence a 0.15 eV reduction of the 4f surface shift is predicted, from 0.6 eV, as measured on the Ce $5p_{3/2}$, to ~ 0.45 eV. In case of γ -Ce a similar analysis, as reported in Ref. 9, gives a reduction of the SCS of ~ 0.30 eV resulting in an expected 4f surface shift of the order of 0.2 eV. The results of these calculations are in good agreement with the present experimental findings on the magnitude of the 4f surface shift for CeAl and γ -Ce and seem to indicate that, as far as the relation between the f^1/f^0 intensity ratio and the f^0 hybridization shift is concerned, the AIH model gives a satisfactory description of the underlying physics. On the other hand, with most of the f^1 spectral weight being located at E_F , due to its Kondo-like origin, no f^1 surface shift is predicted by theory, consistent with the experimental results.

It has to be noted that according to the AIH model the magnitude of the hybridization shift of the f^0 final state depends critically on the density of the other extended states in the relevant energy range.² In order to directly relate the f^0 hybridization shift to T_K , it is important therefore to ensure that no significant variations occur in the mentioned non- f

density of states (DOS) on going from the bulk to the surface. As discussed, the non- f DOS may be probed in off-resonance conditions for both the Ce $3d$ and $4d$ thresholds giving bulklike and surfacelike profiles, respectively. The off-resonance spectra of CeAl are compared, after a broadening of the $4d$ off-resonance spectrum accounting for the different resolutions, in the inset of Fig. 2. Their strong similarity rules out any possible artifact due to a dependence of the surface-to-bulk f^0 shift on modulations of the non- f DOS. Similar results have been obtained for γ -Ce.

It is interesting to note that while the magnitude of the $4f$ surface shift decreases with T_K up to intermediate hybridizations (as in γ -Ce), according to the results of the AIH calculation, the surface shift would increase again with an inverted sign (i.e., with the bulk f^0 peak at larger binding energy compared to the surface f^0 peak) in cases of larger hybridizations. For α -Ce (bulk $T_K \sim 1000$ K) the variation of the hybridization shift between surface and bulk thus overcompensates the SCS with a total $4f$ surface shift of ~ 0.2 eV.⁹ Unfortunately in these cases the weak f^0 bulk intensity is largely obscured by the nearby overwhelming f^1 signal and a quantitative analysis of the $4f$ surface shift may be difficult to achieve. We mention anyway that previous results on α -Ce have been fitted^{8,9} with the bulk f^0 peak at slightly larger binding energy or just overlapped to the surface f^0 signal, somewhat suggesting the same trend indicated by theory.

As a last point, we note that only very recently²⁰ $4f$ SCS's have been studied on elemental monocrystalline R 's, giving values systematically smaller than those previously reported

on polycrystals. This implies that the absolute magnitude of the SCS as obtained from polycrystals may be somewhat different from the ones related to a well defined surface, even in cases of R compounds. However, this important aspect does not affect the present analysis on the nature of the Ce $4f$ surface shift which is based on the apparent internal inconsistency between the results on Ce $4f$ and the other core levels. We have in fact shown here how the mechanism of hybridization between the $4f$ states and the continuum influences the magnitude of the Ce $4f$ surface shift with respect to the usual SCS found for (unhybridized) core levels, despite its value.

In conclusion, by exploiting RPE at the Ce $4d \rightarrow 4f$ and $3d \rightarrow 4f$ thresholds, the nature of the Ce $4f$ surface shift is analyzed providing an important test to the predictions of the AIH model. We show that only for small values of the $4f$ hybridization (bulk $T_K \sim 20$ K, or lower), as in CeAl, do the $4f$ levels behave as the other core levels and a $4f$ surface shift can be detected. On the other hand, for larger hybridizations (bulk $T_K \sim 100$ K), as in γ -Ce, the decreased surface coordination is responsible for a surface hybridization shift which compensates the SCS in such a way that a smaller surface shift (≤ 0.2 eV) is observed. Good agreement of the experimental results is found with the prediction of the AIH concerning the magnitude of the hybridization shift of the Ce $4f^0$ ionization feature.

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