Electronic surface and bulk contributions to core-level XPS, XAS and BIS in $CePd_7$ compounds

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Abstract. We present a new theoretical analysis of various spectroscopic data (3d XPS, 2p XAS and BIS) of CePd$_7$ compounds within the impurity Anderson model by using a consistent set of parameters and by taking into account, when needed, both bulk and surface contributions. Actually in this paper we restrict the calculation of the surface contribution to the most surface sensitive technique, i.e. the 3d XPS spectrum. The parameter values for the bulk contribution are chosen so as to obtain the best fit to the 2p XAS spectrum, which is the less surface sensitive spectrum. The present analysis gives a general satisfying accord with the three kinds of experiment, provided that a surface contribution, from almost γ-like Ce, up to 37.5%, is included in the 3d XPS spectrum of CePd$_7$, whereas only a bulk contribution is assumed for 2p XAS and BIS.

1. Introduction

High-energy spectroscopies play a prominent role in the investigation of the Ce valence in various Ce compounds [1–4]. Among Ce intermetallics, the case of CePd$_7$ is certainly exceptional, to begin with its thermodynamical and magnetic properties are exceptional. More precisely, very low linear specific-heat coefficient as well as very low Pauli-like susceptibility [5] are consistent with highly delocalized 4f orbitals in CePd$_7$ in contrast to other Ce compounds [6]. Moroever, quite recently [7], a standard LMTO band-structure calculation, including a strong Pd 4d–Ce 4f hybridization, provided a rather good description of the density of states at the Fermi level of CePd$_7$ and a qualitative agreement with the corresponding BIS spectra. However the occurrence of satellites in core-level spectra also indicated a fairly strongly correlated nature of the 4f states in CePd$_7$. Because of the localized character of the core hole, core XPS and XAS essentially reflect the 4f contributions at the Ce sites in the final states and have recently been interpreted within the framework of the impurity Anderson model in a preliminary fashion [7]. In the analysis of [7] the set of parameter values was obtained by the best fit to the experimental 3d XPS spectrum of CePd$_7$. However, using that model, it is quite difficult to fit simultaneously 3d XPS, 2p XAS and BIS spectra, with the help of a unique set of parameters, at least as long as only the bulk electronic structure of CePd$_7$ is considered [7].

Generally speaking, it is well known that (i) Ce at the surface of a mixed-valency Ce intermetallic has a tendency to exhibit almost a 4f^1 configuration (γ-like Ce) and (ii) the three previously considered spectroscopic techniques present quite different surface sensitivities. Especially the measure of ejected electrons from primary processes, such as core XPS,

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is intrinsically surface sensitive and may be used for the experimental study of surface physics [8]. In this paper we first recall the impurity Anderson model (section 2). Then within that model we analyse the Ce 2p XAS spectrum of CePd$_7$ with the help of only a bulk contribution since core XAS is rather surface insensitive (section 3). The best fit to the experimental 2p XAS data provides the bulk parameters (section 3), whereas the surface parameters are chosen such as to correspond to almost γ-like Ce (section 4). Moreover the 3d XPS spectrum with an Al Kα source is interpreted as a superposition of 62.5% bulk and 37.5% surface contributions (section 4). The experimental BIS spectrum is analysed by only a bulk contribution (section 5). Finally a discussion and concluding remarks are given in section 6.

2. The model Hamiltonian

In this paper we present a new theoretical analysis of 3d XPS, 2p XAS and BIS for CePd$_7$ compounds within the impurity Anderson model. For 3d XPS, we assume that some parameters entering the Hamiltonian of the bulk system are different from those of the surface and we superimpose the two contributions. For 2p XAS and BIS we will only take into account the bulk contribution within a unique set of bulk parameter values. The Hamiltonian of the system is written as

$$H = \sum_{k,\nu} \varepsilon_{4d}(k) a_{4d}^+(k,\nu) a_{4d}(k,\nu) + \sum_k \varepsilon_{5d}(k) a_{5d}^+(k) a_{5d}(k) + \varepsilon_f^0 \sum_\nu a_f^+(\nu) a_f(\nu) + \varepsilon_c a_c^+ a_c$$

$$+ \frac{V}{\sqrt{N}} \sum_{k,\nu} [a_{4d}^+(k,\nu) a_f(\nu) + \text{HC}] + U_{ff} \sum_{\nu > \nu'} a_f^+(\nu) a_f(\nu) a_f^+(\nu') a_f(\nu')$$

$$+ \frac{U_{fd}}{N} \sum_{k,k',\nu} a_f^+(\nu) a_f(\nu) a_{5d}^+(k) a_{5d}(k') - (1 - a_c^+ a_c) U_{fc} \sum_\nu a_f^+(\nu) a_f(\nu)$$

$$- (1 - a_c^+ a_c) \frac{U_{dc}}{N} \sum_{k,k'} a_{5d}^+(k) a_{5d}(k').$$

In the preceding Hamiltonian, $\varepsilon_{4d}(k)$, $\varepsilon_{5d}(k)$, ε_f^0 and ε_c are the energies of the Pd 4d valence-band, Ce 5d conduction-band, Ce 4f and core levels, respectively; $a_{4d}^+(k)$, $a_{5d}^+(k)$, $a_f^+(\nu)$ and a_c^+ are the corresponding electron creation operators, k denoting the index of the energy level ($k = 1, \ldots, N$) in both the valence and conduction bands [7] and ν specifying both the spin and orbital degeneracies ($\nu = 1, \ldots, N_f = 14$). The hybridization between the Ce 4f and the Pd 4d states is called V. In the three last terms of the Hamiltonian, U_{ff} is the Coulomb interaction between 4f electrons, whereas $-U_{fc}(-U_{dc})$ is the core-hole potential acting on the Ce 4f electron (Ce 5d electron); the subscript c means 3d for XPS and 2p for XAS. Let us notice that in the case of BIS, $a_c^+ a_c = 1$, both in the initial and final states. In the calculation we confine ourselves to the subspace containing 4f^0, 4f^{1}L and 4f^{2}L^2 configurations in the ground state where L labels a hole in the 4d valence band. The realistic bands of CePd$_7$ in [7] are replaced by finite numbers of levels [7] corresponding to rectangular densities of states as shown in figure 1. The energy band calculation (figure 1 (bottom panel)) shows that the Pd 4d band is almost filled and the Ce 5d band is mainly unfilled, so we assume, for simplicity, that $\varepsilon_{4d}(k)$ is a filled valence band and $\varepsilon_{5d}(k)$ is an empty conduction band with the Fermi energy ε_F at the top (bottom) of $\varepsilon_{5d}(k)(\varepsilon_{4d}(k))$, as shown in figure 1 (top left). Using the preceding Hamiltonian we give,
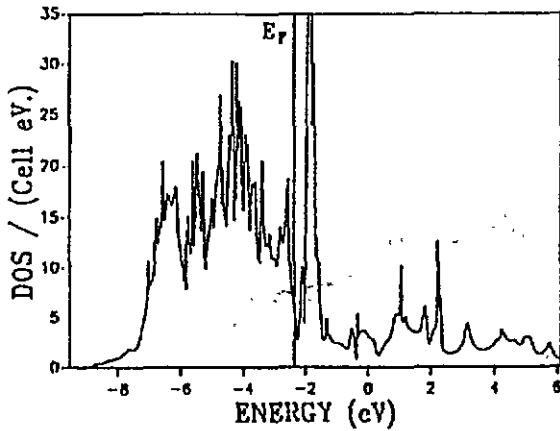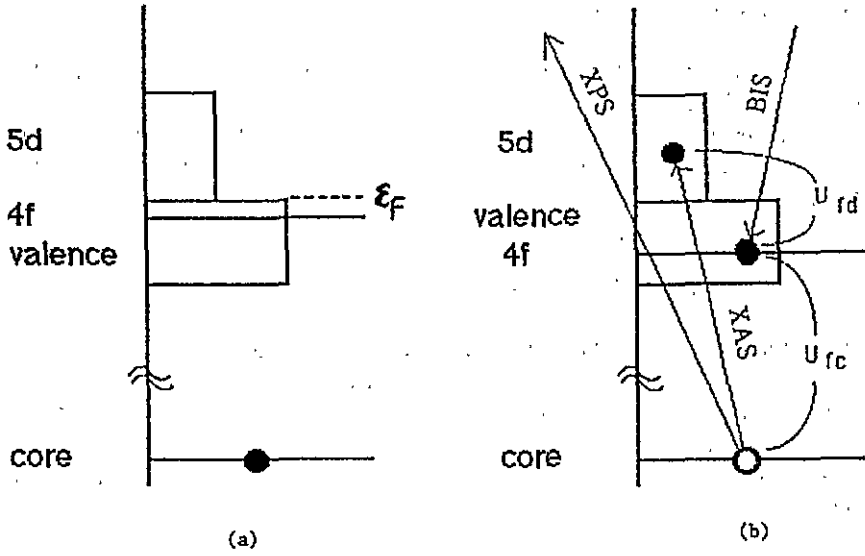
Figure 1. A schematic core-level, valence Pd 4d and Ce 4f and 5d band structure of CePd₇, mimicking a realistic LMTO band structure (lower panel) (see [7]) in the ground state (top left). The mechanism of core XPS, XAS and BIS in the final state is shown top right.

in the next sections, our numerical results for 2p XAS, 3d XPS and BIS spectra for CePd₇ compounds (see figure 1 (top right)) where the final states of the different spectroscopies are schematically presented. In all corresponding spectra, we will introduce the following Lorentzian function: $L(X) = \Gamma/[\pi(X^2 + \Gamma^2)]$ where Γ is the spectral broadening.

3. Analysis of the 2p XAS spectrum

The core absorption spectrum is rather surface insensitive and so we will only consider the bulk contribution to the 2p XAS (often called the L_{II} or L_{III} XAS) spectrum of $CePd_7$. When a 2p core electron is absorbed into the conduction Ce 5d states (figure 1 (top right)), then $a_c^+ a_c = 0$ (*c* represents 2p) and the system state $|g\rangle$ of energy E_g changes to the final state $|f(XAS)\rangle$ of the 2p XAS with the energy $E_f(XAS)$. The absorption spectrum is

$$F_{XAS}(\omega) = \frac{1}{N} \sum_f \left| \langle f(XAS)| \sum_k a_{5d}^+(k) a_c |g\rangle \right|^2 L(\omega - E_f(XAS) + E_g).$$

Our numerical result (bulk only) is given in figure 2 and we chose our parameter values to obtain the best fit to the experimental data [7]. Especially $\Delta = \varepsilon_f^0 - \varepsilon_F = -0.7$ eV, where ε_F is the Fermi level and the hybridization $V = 0.6$ eV. With the present set of (bulk) parameter values we found the average 4f electron number $n_f = 0.57$ (see table 1). All the other parameters are given in table 2 of [7]. The background contribution (dashed curve) is taken into account in the same way as [7].
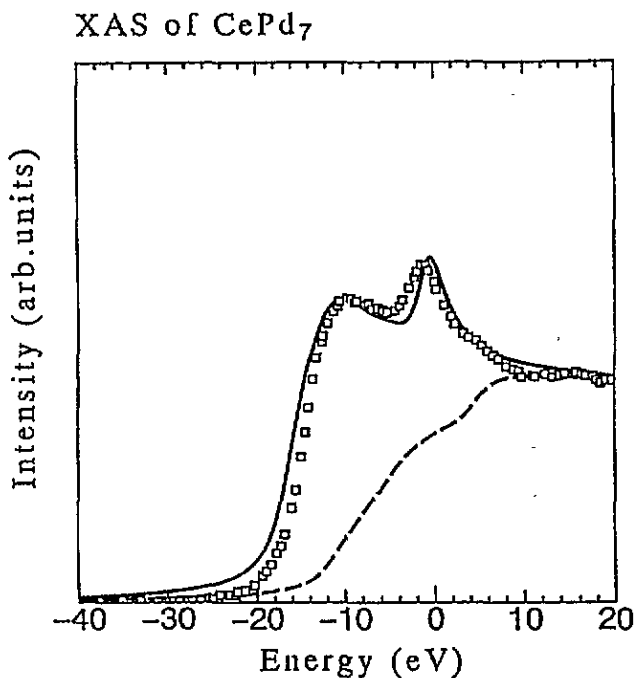
XAS of CePd₇

Figure 2. The calculated Ce 2p XAS of $CePd_7$ (solid line) including a background contribution (dashed line) and compared to the experimental data (small squares).

4. Surface and bulk contributions to the 3d XPS spectrum

As compared to 2p XAS, the Ce core XPS spectrum is very surface sensitive, so we need to analyse the experimental 3d XPS of $CePd_7$ [7] within a superposition of both bulk and

Table 1. Surface and bulk values of the parameters Δ and V. The calculated average 4f electron number, n_f, is also given for the surface and the bulk. All the other parameter values are taken from table 2 of [7].

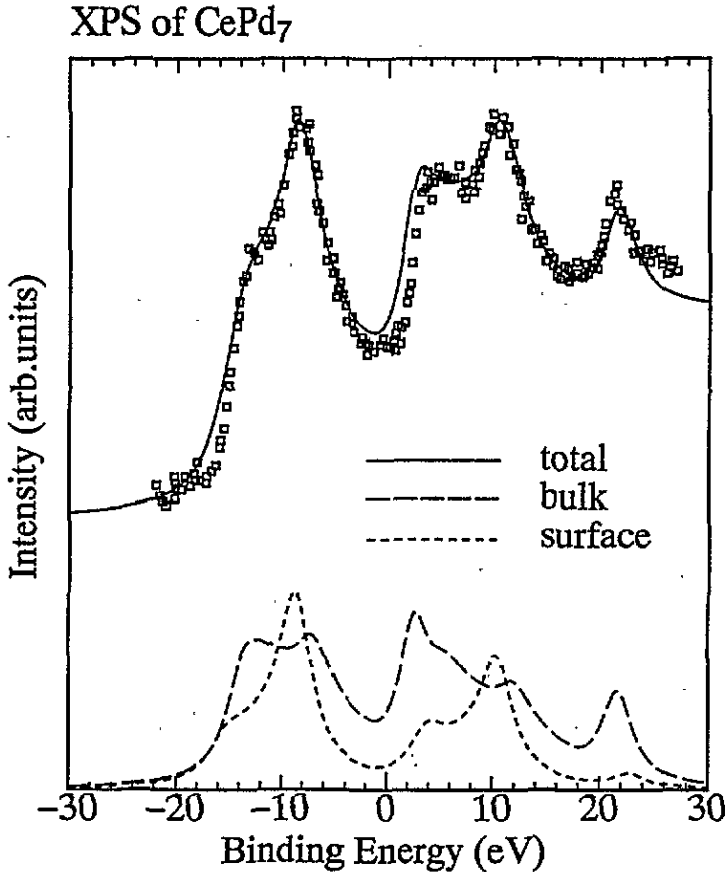|	Surface	Bulk
Δ (eV)	-2.5	-0.7
V (eV)	0.4	0.6
n_f	0.94	0.57

XPS of CePd₇

Figure 3. The calculated Ce 3d XPS of CePd₇ (solid line) compared to the experimental data with an Al Kα source (small squares). The total 3d XPS spectrum is decomposed into bulk (dashed line) and surface (dotted line) contributions.

surface contributions. After the absorption of an incident photon, when a 3d core electron is excited to a high-energy photoelectron state, $a_c^+ a_c = 0$ and the ground state $|g\rangle$ changes to the final state $|f(\text{XPS})\rangle$ with the energy $E_f(\text{XPS})$. The corresponding 3d XPS spectrum is given by

$$F_{\text{XPS}}(E_B) = \sum_f |\langle f(\text{XPS})|a_c|g\rangle|^2 L(E_B - E_f(\text{XPS}) + E_g).$$

Essentially, we suppose that the 4f level ε_f^0 and the hybridization V for a Ce atom at the surface ($\Delta = \varepsilon_f^0 - \varepsilon_f = -2.5$ eV; $V = 0.4$ eV) are different from those obtained (section 3)
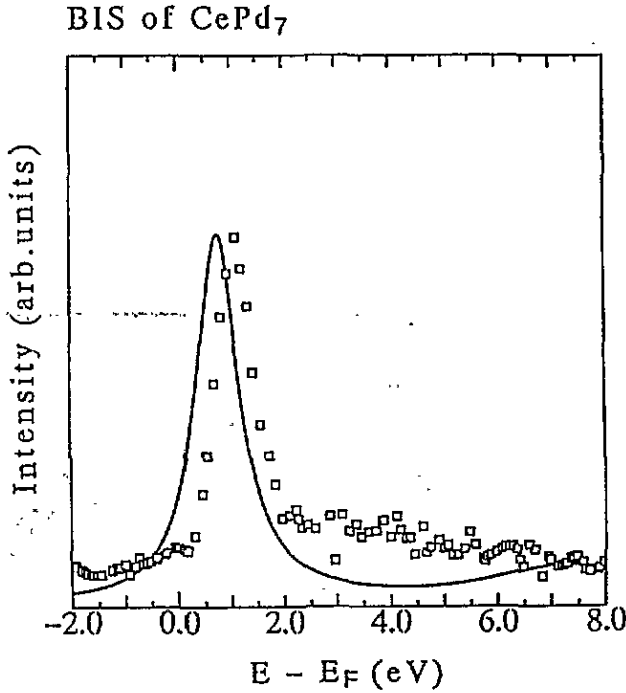
BIS of CePd$_7$

Figure 4. The calculated BIS of CePd$_7$ (solid line) compared to the experimental data obtained at a fixed photon energy of 1487 eV (small squares).

for the bulk (table 1). Within the 'surface' parameters, the n_f electron number is close to one, as it should be ($n_f = 0.94$ instead of 0.57 found for the bulk). Actually the parameters for the surface part have been taken so that the Ce system is almost in the trivalent state ($\sim 4f^1\gamma$-like Ce). We show (figure 3) the decomposition of 3d XPS into the surface and bulk contributions. For a comparison to the experimental spectrum [7] we superpose the surface and bulk spectral intensities with the weights: surface/bulk=0.6/1.0 (figure 3). Also, the total spectrum (solid curve) includes a background contribution in a similar way as in [7]. The corresponding average 4f electron number is then $n_f = 0.75$ (close to the value of 0.73 in our previous bulk-restricted calculation [7]). In the present calculation we have a surface contribution of 37.5% to the total 3d XPS spectrum.

5. Analysis of the BIS spectrum

For the BIS process the surface sensitivity is more questionable. Here we assume only a bulk contribution for simplicity. When one incident electron is added to the f level (figure 1(b)), the system state changes to the final state $|f(\text{BIS})\rangle$ of the BIS with energy $E_f(\text{BIS})$ and the corresponding spectrum is

$$F_{\text{BIS}}(E) = \sum_f \sum_\nu |\langle f(\text{BIS})|a_f^+(\nu)|g\rangle|^2 L(E - E_f(\text{BIS}) + E_g)$$

where we have disregarded the creation of a Ce 5d electron ($a_{5d}^+(k)$) in the BIS process. For the broadening Γ of the Lorentzian function, we assume $\Gamma = \Gamma_0 + \Gamma_1|E - \varepsilon_F|^2$ as in [7].
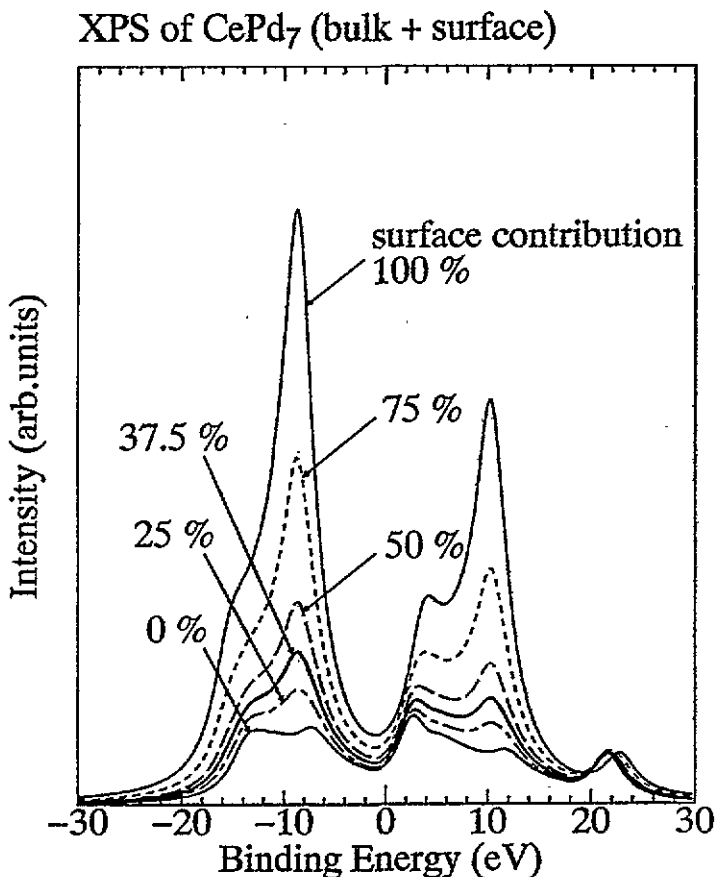
Figure 5. The calculated Ce 3d XPS of CePd₇ with different weights of the surface contribution.

Figure 4 exhibits our calculated spectrum with the same parameter values as in section 3. Especially we find a BIS peak at about 0.7 eV from the Fermi level ε_F without satellite structure at near energy in better agreement with the experimental data than in [7].

6. Discussion and concluding remarks

Our results show that if we assume a considerable surface contribution (more than one-third) to 3d XPS, but only a bulk contribution to 2p XAS and BIS, then the agreement between the theoretical and experimental results is much improved compared to our previous results [7] (only bulk consideration). From an experimental point of view, it is interesting to change the surface sensitivity of 3d XPS by changing the incident photon energy or the angle of the emitted electron (see [9] and references therein, [10]) and that of BIS by changing the angle of the incident electron. With our model calculation, we can predict the change of 3d XPS and BIS spectra with the change of the surface contribution as shown in figures 5 and 6, respectively. In figure 5, the intensity of the highest-binding-energy peak (4f⁰ final state) is normalized to be constant. (The background contribution is not included here.) It is found that with increasing surface contribution the relative intensity of the peaks at
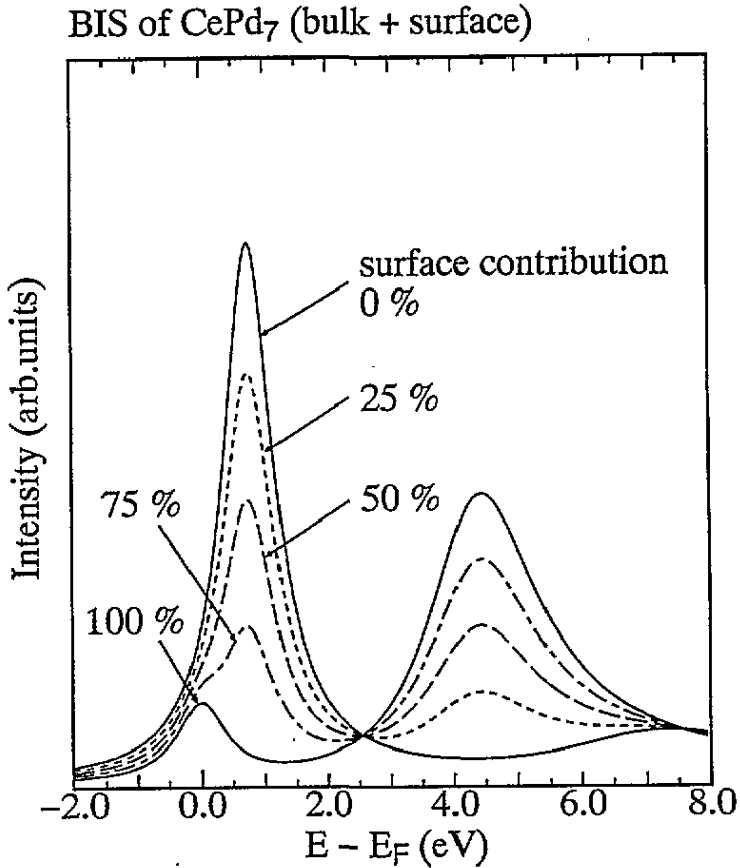
Figure 6. The calculated BIS of CePd$_7$ with different weights of the surface contribution.

$E_B \approx 10$ and -9 eV increases. From figure 6, we find that the relative intensity of the peak at $E - \varepsilon_F \approx 4.5$ eV increases with increasing surface contribution. It is highly desirable that these results are checked experimentally in the near future.

Acknowledgments

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