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Localization of screening orbitals, local-environment effects, and intermediate valence in core-level spectroscopy: Ce vs Tm

A. Bianconi
Istituto di Fisica, Universitá di Roma, I-000185 Roma, Italy

M. Campagna
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

S. Stizza
Istituto di Fisica, Universitá di Camerino, I-62032 Camerino, Italy

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We have studied the x-ray absorption spectra (XAS) at the L_3 and L_1 absorption edges of metallic γ-Ce, $CeCu_2Si_2$, $CePd_3$ and compared with those of Tm metal and intermediate valence TmSe. We analyze the x-ray absorption near edge structure (XANES) taken at high signal-to-noise ratio and high resolution using synchrotron radiation at the facility PULS in Frascati with respect to (1) energy shifts of core-level transitions due to $4f$ electron screening, (2) determination of the local character of the $5d$ final states and mixing of the $5d$ with $6s,p$ orbitals near the Fermi level, and (3) use of the XANES as a microscopic tool to determine the intermediate valence in mixed-valence rare-earth-metal compounds. It is concluded that while for the heavy rare earths, $Z >$ Sm, the XANES gives direct information on the intermediate valence, in Ce the occupancy of the $4f^0\,(5d,6sp)^4$ configuration is underestimated by about a factor 5 to 6 in favor of the $4f^1(5d,6sp)^3$ configuration.

I. INTRODUCTION

The use of x-ray absorption spectroscopy (XAS) to investigate the electronic structure of intermetallic compounds has recently regained interest because of the work of Launois *et al.*[1] and Martin *et al.*[2] on TmSe and $Sm_{0.75}Y_{0.25}S$, respectively. Those authors showed that the structure near the L_3 edge ($2p$ to $\overline{5,\epsilon d}^*$ transitions) can be used to obtain quantitative information on the intermediate valence (IV) (from the near edge structure) and on the coupling of valence fluctuations to the phonons [from the extended x-ray absorption fine structure (EXAFS)]. More recent work by Bauchspiess *et al.*[3] and Krill *et al.*[4] on Ce intermetallic and insulating compounds showed that in the case of Ce a straightforward determination of the intermediate valence v from the x-ray absorption amplitudes may lead to erroneous conclusions (e.g., CeO_2, an f^0 system in the ground state, which also shows "two L_3 peaks", would be classified as an IV compound).

We compare here XAS data of γ-Ce, $CeCu_2Si_2$ (formally f^1 systems in the ground state), and $CePd_3$, a prototype IV Ce compound, with XAS data of trivalent (f^{12}) Tm metal and IV TmSe. We deduce that a major so-called change in f mixing in the final state after photoabsorption *occurs (primarily) for the local* $4f^0$ *configuration.* This change is so large that for a system formally in the f^0 configuration in the ground state, e.g., CeO_2 with valence $v \cong 4$ ($f \cong 0$) in the ground state, one obtains $v \cong 3.4$ ($f \cong 0.6$) after photoabsorption. In contrast, we deduce that this "f-count change" *in XAS* is much smaller, i.e., not larger than 10%, for metallic f^n systems with $n \geq 1$. We will therefore suggest that the presence of two-absorption thresholds in *metallic* Ce compounds is indicative of the presence of both f^0 and f^1 configurations in the *initial* state. However, since one expects a transfer of weight from the f^0 to the f^1 configuration which, as we shall see, is about 5 to 6 times larger than the transfer $f^1 \rightarrow f^2$ we have to take this into account when quantitatively estimating the "valence" of Ce. The experiments have been performed in Frascati, using x-ray from the storage ring Adone. Experimental details have been given elsewhere.[5]

II. RESULTS AND DISCUSSION

Figure 1 shows the x-ray absorption near edge structure (XANES) of metallic γ-Ce at both the L_3 and L_1 edges. The zero of the energy scale has been taken at the energy E_1 of the maximum of the derivative of the absorption jump at the L_1 threshold. E_1 is the energy threshold for transitions from core $2s$ electrons to the Fermi level. It is impossible to locate the Fermi level in the L_3 spectrum because of the strong $2p \rightarrow \overline{5,\epsilon d}^*$ "giant resonance" occurring right at the Fermi level. In order to compare the L_3 with the L_1 spectrum on the same energy scale, we have used the criterion of aligning the minimum m of the L_1 EXAFS oscillations with the maximum d of the L_3 EXAFS oscillations (see Fig. 1). This is because we expect a difference of phase $\sim\pi$ between the two EXAFS oscillations.[6] This criterion locates the Fermi level between the derivative maximum E_3 and the main absorption peak of the L_3 spectrum. The same criterion for the energy scale has been used also for the L_3 and L_1 spectra of the Ce compounds shown in Fig. 2. In this figure the spectra of the compounds $CePd_3$ and $CeCu_2Si_2$ have been normalized to the high-energy absorption continuum above 90 eV and the relative absorption has then been plotted. This procedure allows the comparison of the intensities of the peaks between spectra of different samples. *Three regions* can be identified in the absorption spectra of Figs. 1 and 2: (a) the *edge region,* corresponding to an energy range of about 5 eV at the absorption threshold (the shadowed area in Fig. 2); (b) the *XANES region,* extending from the edge region to an energy $E_c = \hbar\omega - E_1 = 151/d^2$; in this region the excited photoelectron has a wavelength larger than the interatomic distance d; (c) the *EXAFS region* at energies higher than E_c, where the photoelectron has a short wavelength (high $\vec{k}$ values).[7]

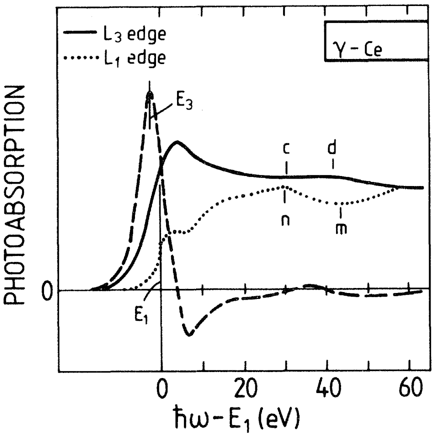

FIG. 1. X-ray absorption at the L_3 and L_1 edges of γ-Ce. The photoabsorption derivative of the L_3 edge is also shown (dashed curve).

A. The edge region: Mixing of 5*d* and 6*sp* orbitals near the Fermi level

Because of dipole selection rules the L_3 (L_1) absorption spectrum of the edge probes the *local* density of states of the d components (p components) of the final states near the Fermi level. Therefore, the comparison of the L_3 and L_1 edges can give information on the mixing of the $5d$ and $6sp$ orbitals. In the edge region the L_1 spectrum is therefore dominated by transitions to delocalized p states at the Fermi level while the L_3 edge is dominated by the giant resonance $2p \rightarrow \overline{5,\epsilon d}^*$. In the $2p$ core transitions to continuum levels it is expected that the final-state d wave function will collapse inside the inner well due to the centrifugal potential acting on the $l=2$ final state. Giant resonances due to the final-state wave-function collapse have been observed in atomic rare earths at the $5p$ core threshold to the $\overline{5\epsilon d}^*$ final state.[8] A similar giant resonance has been observed at the $3p$ threshold of atoms of the first period of transition metals and this resonance is retained in the solid-state spectra.[9] The *atomic* character of the giant reso-

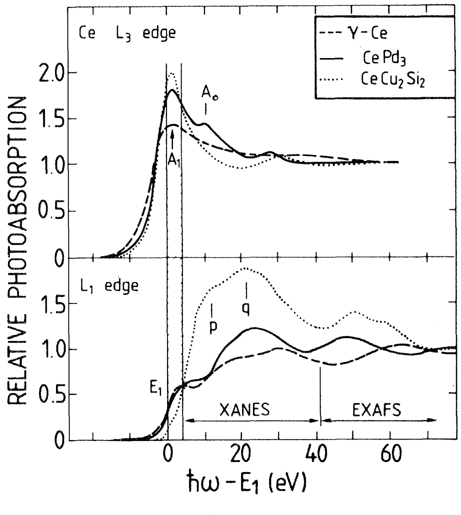

FIG. 2. Comparison of the L_3 and L_1 absorption edges of γ-Ce, $CePd_3$, and $CeCu_2Si_2$, indicating the *edge* region (shadowed area), the XANES, and EXAFS region, respectively.

nance is confirmed by the *energy position* of the maximum, which is at the same energy (± 0.2 eV) in each compound, but *solid-state* effects dominate its *line shape.* As it is shown in Table I the linewidth Γ of this resonance is decreasing from 5.6 eV for γ-Ce to 3.6 eV for $CeCu_2Si_2$. This broadening of the line cannot be ascribed to a chemical shift of the core initial state. In fact, the L_1 edges for all the compounds are at the same energy within ± 0.5 eV. Moreover if one takes the maximum of the derivative of the L_3 spectra one obtains a chemical shift for the Ce compounds which is different than the one observed in x-ray photoemission.[4,10]

Both the *intensity* of the giant resonance, which in $CeCu_2Si_2$ goes from 98% of the atomic absorption at high energy (normalized at 1 in Fig. 2) to 45% in γ-Ce, and its *width* are strongly *medium dependent.* The spectrum of $CeCu_2Si_2$ is significantly different than that of the other compounds. At the L_3 edge the giant resonance is very strong (98% intensity) and sharp and the jump at the L_1 absorption at E_1 is small when compared to that of γ-Ce. We conclude that at the Fermi level the final states are primarily *d-like* in $CeCu_2Si_2$ and that the mixing of the 5*d* with the 6*sp* final states is quite small within an energy range of 4 eV above the Fermi level. In comparison γ-Ce shows a rather weak giant resonance and a large absorption jump at the L_1 edge. This indicates a much larger mixing of states with different symmetry at the Fermi level in γ-Ce.

We note that the same trend is observed when comparing TmSe, TmTe, and Tm metal, see Figs. 3 and 4.[5] Metallic IV TmSe and semiconducting TmTe exhibit a stronger and sharper giant resonance than Tm metal, indicating a weaker mixing of 5*d* with 6*sp* orbitals.[5]

On the other hand, from the comparison of Fig. 3 we deduce that the giant resonance is stronger in Tm than in Ce metal. This provides experimental evidence for an increased localization of the 5*d* final states (smaller hybridization) in going from the light to the heavy rare-earth metals.

B. The XANES region: Enhancement of the local character of the *d* final states by local environment effects

The XANES region is dominated by multiple-scattering resonances of the excited photoelectron inside the neighbor atomic shells.[7,11,12] The intensity of the multiple-scattering resonances is determined by a *joint effect* of the *geometrical distribution* of neighboring atoms, around the absorbing central atom, and of the *type of neighboring atoms* through their photoelectron backscattering amplitude at low values of wave vector $\vec{K}$ of the photoelectron. Our data show that these conditions are satisfied in the case of $CeCu_2Si_2$ at the L_1 edge, where strong peaks *p* and *q* appears in the XANES region (see Fig. 2). These peaks arise from multiple-scattering resonances of the initially excited *p* photoelectron which is backscattered by Si and Cu neighbors. The final-state wave function at the resonance energy is strongly localized inside a molecular cluster around the central Ce atom. If strong multiple-scattering resonances appear at the L_1 edge, they should be expected also at the L_3 edge of the same atom. However, at the

TABLE I. Transition energies, linewidth, and splittings of the L_3 edge of Ce in γ-Ce, $CePd_3$, $CeCu_2Si_2$, and Tm in Tm metal and mixed - valent TmSe.

L_3 edge	Derivative maximum E_3 (eV)	Absorption maximum A_1 (eV)	Linewidth $\Gamma = A_1 - E_3$ (eV)	A_1/μ_0[a] relative intensity	Splitting of absorption maxima Δ	Splitting of derivative maxima δ
γ-Ce	5720.5	5726.1	5.6	1.45		
$CePd_3$	5722.5	5726.1	3.6	1.8	$\Delta = 9.4$ eV	$\Delta = 11.6$ eV $\delta = 4$ eV
$CeCu_2Si_2$	5722.5	5726.1	3.6	1.98		
Tm metal	8648.8	8654	5.2	1.52	~ 7	~ 7
Tm^{3+} in TmSe	8651.2	8654	2.8	2.0	~ 7	~ 7

[a] μ_0 is the atomic absorption background in the EXAFS region.

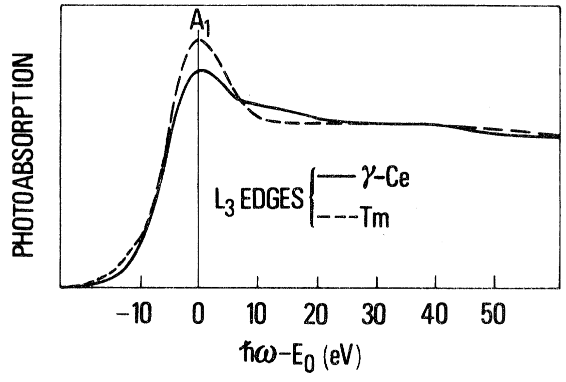

FIG. 3. Comparison of L_3 absorption edge of γ-Ce and Tm metal.

L_3 edge the multiple-scattering resonances are due to the *d* channel of the photoionization, therefore they will be located at different energies. The anomalous intensity of the A_1 giant resonance in $CeCu_2Si_2$ is therefore explained by the local character of the final state enhanced by the multiple scattering inside the molecular potential of neighboring atoms, like the resonances in the L_1 XANES of the same system.

The amplitudes of the XANES are coupled to the degree of hybridization of the states above the Fermi level. In γ-Ce both the L_1 XANES and the giant resonance are very weak. This confirms further that the final states are mostly *delocalized in γ-Ce* and a large mixing of the orbitals of 5*d* and 6*sp* symmetry occurs. From Fig. 2 we deduce that the case of $CePd_3$ is intermediate between that of γ-Ce and $CeCu_2Si_2$.

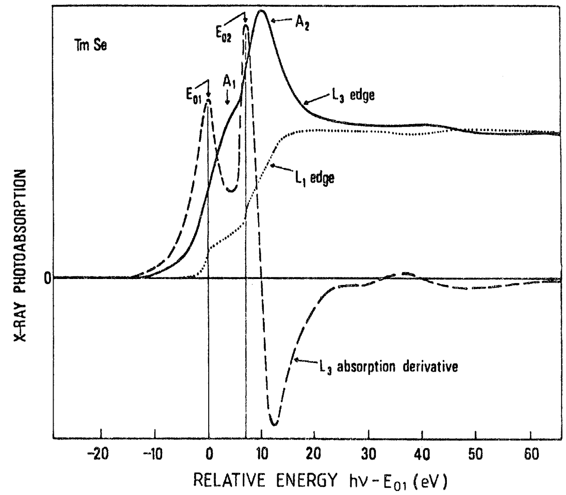

FIG. 4. X-ray absorption at the L_3 edge of IV TmSe and photoabsorption derivative indicating the IV state of Tm (two L_3 edges) in this selenide.

C. The intermediate valence of $CePd_3$ and the effect of core-hole induced relaxation

The L_3 edge of $CePd_3$ in Figs. 2 and 5 shows an anomalous peak A_0 which is not present in the other compounds. A jump in the absorption coefficient appears in the L_1 spectrum at the corresponding energy. We ascribe these features as due to the intermediate valence of $CePd_3$, where in the ground state the Ce atoms resonate between the $2p^64f^0(5d,6sp)^4$ and the $2p^64f^1(5d,6sp)^3$ configurations. The peaks A_1 and A_0 are therefore assigned as originating from the final states $2p^54f^1(5d,6sp)^3\,\overline{5,\epsilon d^*}$ and $2p^54f^0(5d,6sp)^4\,\overline{5\epsilon d^*}$. We have plotted in Fig. 5 the high-resolution spectrum of $CePd_3$ with its derivative. The derivative spectrum shows a third, comparatively small structure in the low-energy side of the absorption threshold. We identify this structure as the $4f^2$ final state of the Ce atom after the switching on of the core hole. In

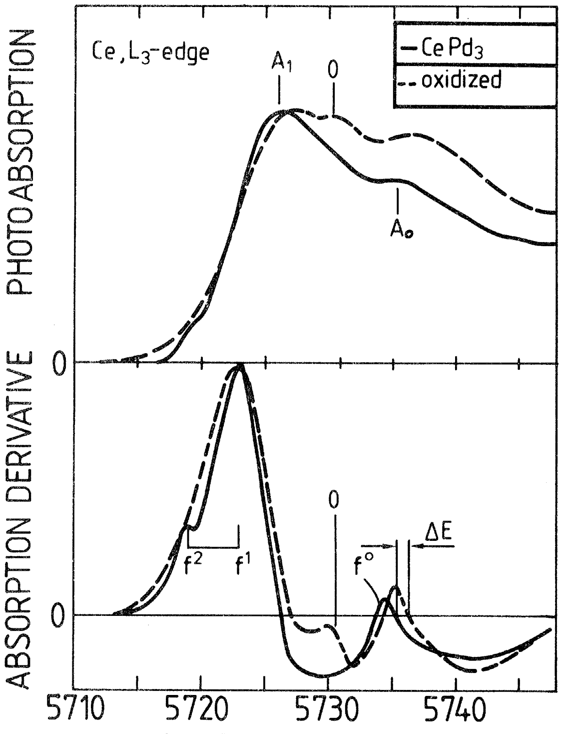

FIG. 5. L_3 edge of clean and air-oxidized IV $CePd_3$. The photoabsorption derivative (lower part) indicates the final state f^0, f^1, and f^2 after photoabsorption in the clean IV $CePd_3$.

the language of Fuggle *et al.*[13] this feature corresponds to the "well-screened" relaxed peak observed also in the x-ray photoelectron spectroscopy (XPS) spectra of $3d$ core levels of intermetallic Ce compounds.

The photoionization of an inner shell causes rearrangements (relaxation) of the valence states at the atomic site of the core hole. In the presence of the hole the more atomiclike $4f$ states are attracted in a different way than the other delocalized states. Two types of core-hole screening are therefore possible: one where an extra electron occupies the $4f$ level resulting in the well-screened final state, the other where the usual screening occurs through conduction electrons, i.e., in the sense of a Friedel impurity screened by conduction electrons.

If the identification of the features of Fig. 4 as the f^2, f^1, and f^0 final-state configurations in the same L_3 spectrum of $CePd_3$ is correct then we have to conclude that the partial relaxation with subsequent filling of the $4f$ state takes place during the lifetime of the excited state. This process is obviously typical for *Ce compounds involving the* $4f^0$ *configuration in the ground state.*

Interestingly, the peaks A_1 and A_0, i.e., the doublet structure, are absent in the XAS of trivalent CeF_3,[14] but are present in the XAS spectra of CeO_2 and CeF_4, formally f^0 systems in the initial state. A puzzling question is still why the separation $A_1 - A_0$, 9.5 eV, in metal $CePd_3$ is apparently much larger than the separation of the same peaks f^1 and f^0 in CeO_2, which is about 6 eV.[4] A larger splitting, $\delta \sim 11$ eV, we remember, occurs in the XPS $3d$ spectra $3d_{5/2}(f^0)$-$3d_{5/2}(f^1)$ of $CePd_3$.[10] In XAS of CeO_2 and CeF_4 (Refs. 4 and 14) the f^0/f^1 intensity ratio is $\sim$ 2:3 which means that in these *insulating* materials the f^1 final state is occupied $\sim$ 66% more often than the f^0 state. In contrast, in metallic $CePd_3$ we see the intensity of the f^2 well-screened peak is at maximum about 10% of the main A_1 peak. This is also in agreement with recent XAS measurements of CeTe,[15] a d^1 metal, which shows only one L_3 edge and have formally the f^1 configuration in the ground state. Here too obviously the f count does not change significantly from the initial to the final state in XAS. So we conclude that a major enhancement of the f^1 signature occurs in the XAS final state. In applying this to $CePd_3$ we conclude that in the initial state the f^0/f^1 ratio had to be 0.4/0.6, i.e., implying a Ce valence of $v = 3.6 \pm 0.1$. This value comes much closer and it tends to exceed the one deduced from lattice constant systematics and neutron scattering, $v \simeq 3.4$.[16]

The energy shift of the transition giving peak A_1 by decreasing the number of $4f$ electrons by 1 can be as large as ~ 9.4 eV because of the large localization of the $4f$ orbitals well inside the radius of the $\overline{5,\epsilon d}^*$ final state. The shift of the transitions giving the peak A_0 upon changing the number of delocalized $5d$, $6sp$ electrons is much lower (~ 1 eV) due to the location of most of the charge of these extended states outside the radius of the quasilocalized $\overline{5,\epsilon d}^*$ final-state orbital.

D. The effect of oxidation on $CePd_3$

The spectrum of $CePd_3$ oxidized by heating the sample in air is also shown in Fig. 5. The sample is expected to contain primarily a mixture of $CePd_3$ and Ce_2O_3 and probably some CeO_2. Upon oxidation both A_1 and A_0 peaks broaden. The f^2 peak of $CePd_3$ seems to disappear completely. A clear shift of the A_0 peak (due to the f^0 configuration) $\Delta E = 0.8$ eV is observed. Also the peak A_1 shifts at higher energies by $\sim$ 0.8 eV. The A_0 peak in the oxidized spectrum is expected to be due to the core transition in the ground state $4f^0(5d,6sp)^0$ of Ce^{4+}. The shift towards higher energy of the peak is assigned to the decrease of the core screening by the $5d$ and $6sp$ empty orbitals. The peak 0 at 6 eV below the A_0 peak of the oxide observed in the CeO_2 spectrum[4] can be related with the relaxed state of CeO_2, the $2p^5 4f^1 (5d,6sp)^0 \overline{5,\epsilon d}^*$ state [13] or due to the $2p$ excited state of Ce_2O_3 $2p^5 4f^1 (5d,6sp)^0\ \overline{5,\epsilon d}^*$ which have the same configuration. It is clear from this figure that the splitting of f^0 and f^1 configurations in the insulating CeO_2 ($\Delta = 6$ eV) is much smaller than that in metallic $CePd_3$ ($\Delta = 9.4$ eV).

E. Light versus heavy rare earths:
Ce vs Tm

When going to the heavy rare-earth compounds the $4f$ bandwidth W becomes very narrow and the intra-atomic splitting U_{eff} increases. Well-screened peaks in metallic systems in XAS are not observed any more, even in XPS for $z >$ Sm.[17] In IV TmSe (Fig. 4) the valence determined by the Tm L_3 absorption edge is $v \cong 2.6$, i.e., close to that measured by direct $4f$ photoemission.[18] Obviously for the heavy rare earths both direct 4*f* and core-level photoemission as well as XAS can be used to determine *v*. This has been recently shown to be true for XPS, even as a function of temperature for the system $EuCu_2Si_2$.[19]

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