

f-count effects in x-ray-absorption spectra of the 3*d* levels in Ce and its intermetallic compounds

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The 3*d* x-ray-absorption spectra of Ce, CeSn₃, CeAu, CePd, Ce₃Pd₅, CePd₃, CeNi₂, and CeNi₅ have been studied. Results of theoretical calculations of the 3*d* absorption spectra are also reported. Comparison with theory shows that the observed spectra are compatible with photoemission-derived 4*f*-level widths, arising from hybridization with the conduction states, of 30–130 meV and *f* counts greater than 0.8, in all the compounds studied. The relative merits of x-ray-absorption spectroscopy as a tool for the study of Ce compounds are briefly discussed.

INTRODUCTION

The role of the 4*f* levels in Ce and its compounds is not the same as in most other lanthanides.^{1–4} They are clearly not so strongly localized and it is more difficult to treat them theoretically than the very strongly localized levels in, for instance, Gd and its compounds. There is thus a special need for experimental studies of the Ce 4*f* levels. Indeed, in the last few years there has been a veritable boom in valence-band photoemission (see, e.g., Refs. 5–16) core-level x-ray-photoemission (XPS) (Refs. 17–25) and x-ray-absorption spectroscopy (XAS) at the 2*p* edges,^{21,22,26–28} with the aim of deducing the number of Ce 4*f* electrons and the strength of their interaction with the other conduction electrons. In this paper we report the measurements and analysis of the 3*d* absorption spectra of La and Ce compounds. These spectra have not been extensively studied before.^{29,30} However, they are of interest because the binding energy of the 3*d* levels permits both XPS and XAS studies, so that it is possible to clarify the influence of multiplet effects on the fine

structure.³⁰ Our purpose here is to show how the shape of the absorption edges can be related to the *f* counts and the hybridization of the *f* levels with the other conduction states. For the analysis we use a theory³¹ which describes both the XPS and the 3*d* XAS spectra. In an earlier study³² of the XPS line shape, we estimated the strength of the hybridization of the *f* level and these data are used for the present work.

Previous XAS investigations of the early lanthanides have shown that the 3*d* region is dominated by transitions of the type,

$$3d^{10}4f^n \rightarrow 3d^9 4f^{n+1}.$$

These transitions occur as strong “white lines”³³ approximately 5 eV below the true threshold (edges) arising from excitation of 3*d* electrons to the Fermi level (E_F). The edges cannot be easily identified because the 3*d*→6*s* and 3*d*→5*d* transitions are dipole forbidden and the 3*d*→6*p* intensity is very low because the density of 6*p* states at E_F and the matrix elements are both low compared with 3*d*→4*f*. The energy of the 3*d*→4*f* transition is lower than that

of $3d \rightarrow E_F$ because the large $3d-4f$ Coulomb interaction lowers the $4f^{n+1}$ level by ~ 10 eV with respect to E_F . The final states thus have atomlike or excitonlike character.

XPS investigations have led us to believe that the ground state Ψ of Ce can be described as a mixture of $4f^0$, $4f^1$, and $4f^2$ wave functions (ϕ^0, ϕ^1, ϕ^2) with weights, lying in the ranges

$$0.0 < c_{(f^0)} < 0.25 ,$$

$$0.7 < c_{(f^1)} < 0.95 ,$$

$$0.0 < c_{(f^2)} < 0.05 ,$$

where the c are so defined that

$$\Psi = (c_{(f^0)})^{1/2} \phi^0 + (c_{(f^1)})^{1/2} \phi^1 + (c_{(f^2)})^{1/2} \phi^2 . \quad (1)$$

As a consequence of this, we expect peaks in the Ce $3d$ XAS spectrum corresponding to the transitions $i \rightarrow 3d^9 4f^1$ and $i \rightarrow 3d^9 4f^2$, where i is the initial ground state. These final states should be separated by 4–6 eV, as in XPS, with the $3d^9 4f^2$ state at lower energy. Transitions $i \rightarrow 3d^9 4f^3$ may be present, but we would expect them to be weak. The $3d^9 4f^3$ -state energy should be higher than the f^2 state because of the rapid increase of Coulomb repulsion energy with increasing f count.

THEORETICAL TREATMENT

Ce compounds are often described theoretically in an Anderson impurity model,

$$\begin{aligned} H = & \sum_{k,\sigma} \epsilon_k n_{k\sigma} + \epsilon_f \sum_{m,\sigma} n_{m\sigma} \\ & + \sum_{k,m,\sigma} V_{km\sigma} (\Psi_{m\sigma}^\dagger \Psi_{k\sigma} + \text{H.c.}) \\ & + \frac{U}{2} \sum_{m,\sigma \neq m',\sigma'} n_{m\sigma} n_{m'\sigma'} \\ & + \epsilon_c n_c - (1 - n_c) U_{fc} \sum_{m,\sigma} n_{m\sigma} , \end{aligned} \quad (2)$$

where ϵ_k describes a conduction level, ϵ_f the f level, and V_{km} the hybridization between the two. H.c. is the Hamiltonian conjugate. The f level has spin (σ) and orbital degeneracy (m), and the effective Coulomb interaction U between two f electrons is taken into account. The core level is given by ϵ_c , and U_{fc} is the interaction between the core hole and the f level. We calculate the ground state of (2) variationally. For this purpose we introduce a basis function (0), where all the conduction states below the Fermi energy E_F are filled and the f level is empty. Furthermore, we define sets of states $\Psi_{m\sigma}^\dagger \Psi_{k\sigma} |0\rangle$ and $\Psi_{m\sigma}^\dagger \Psi_{m'\sigma'}^\dagger \Psi_{k\sigma} \Psi_{k'\sigma'} |0\rangle$, with one

and two f electrons, respectively. The functions ϕ^0 , ϕ^1 , and ϕ^2 in Eq. (1) are expressed in terms of these basis functions. The XAS spectrum can be written as

$$I(\omega) = \frac{1}{\pi} \text{Im} \left\langle \Psi \left| \left[T \frac{1}{\omega - i0^+ + E_0(N) - H} T \right] \right| \psi \right\rangle , \quad (3)$$

where

$$T = \sum_{m,\sigma} W_m \psi_{m\sigma}^\dagger \psi_c + \text{H.c.} \quad (4)$$

describes the x-ray-absorption process. The ground-state energy of (1) is $E_0(N)$, and W_m is a dipole matrix element. To calculate (3), we introduce basis functions $|\nu\rangle$, which are the same as above except that they contain a core hole. Inserting $\sum_\nu |\nu\rangle \langle \nu| \approx 1$ on both sides of $[\omega - i0^+ + E_0(N) - H]^{-1}$, the calculation of (3) is reduced to the inversion of a matrix.³² Since this inversion can be performed analytically, the computational effort is modest. We have shown³² that this approach is correct in the limit $N_f \rightarrow \infty$, $\sum_m |V_{km}|^2 = \text{const}$, where N_f is the degeneracy of the f level. For the actual system $N_f = 14$, and the solution of the model (2) is quite accurate.

In the calculation, the parameters V_{km} enter in the combination³²

$$\pi \sum_{k,m} |V_{km}|^2 \delta(\epsilon - \epsilon_k) = f(\epsilon) . \quad (5)$$

We assume a semielliptical band

$$f(\epsilon) = 2V^2 [B^2 - (\epsilon - B_0)^2]^{1/2} / B^2 , \quad (6)$$

where $B = (B^+ + B^-)/2$ and $B_0 = (B^+ - B^-)/2$, and B^+ and $-B$ are the upper and lower band edges, respectively. The value of V determines the strength of the hybridization, and as a typical measure we use the maximum value of $f(\epsilon)$,

$$\Delta = [f(\epsilon)]_{\text{max}} = 2V^2 / B . \quad (7)$$

In the ground state the unhybridized f^2 level is located $U + \epsilon_f$ above the bare f^1 state, where U is assumed to be 6.4 eV. For a given value of Δ , ϵ_f was varied with respect to E_F in order to change the f count and $c_{(f^x)}$ in a systematic way. In the final state the order and energies of the bare f^x levels are changed by the core-hole potential. The bare f^1 level is pulled down an amount U_{fc} , and the separation between the bare f^1 and f^2 levels becomes $|U + \epsilon_f - U_{fc}|$. In the calculations we keep $\epsilon_f - U_{fc}$ constant when ϵ_f is varied, which leads to a modest variation in the separation of the $i \rightarrow f^1$ and $i \rightarrow f^2$ peaks. U_{fc} was varied between 9.6 and 13.8 eV, and for realistic values of $c_{(f^x)}$, we used U_{fc} at

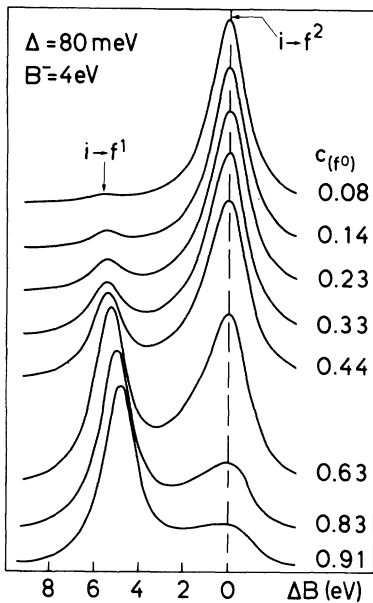


FIG. 1. Calculated XAS absorption spectra at the $3d$ edge of Ce compounds as a function of the f^0 weight c_{f^0} in the ground state. The calculations have been made with 80-meV $4f$ width due to hybridization with the conduction states, and 6.4 eV for the effective f - f Coulomb interaction. After application of a 1.8-eV FWHM Lorentzian broadening, the spectra were normalized to the height of the larger peak and lined up using the $i \rightarrow f^2$ peak.

10 eV. The values of U and U_{fc} are in reasonable agreement with theoretical studies³⁴ and bremsstrahlung isochromat measurements^{11,35} as well as XPS (Refs. 17–25) and other XAS measurements.^{21,22,26–28} Numerous checks were made with different U , U_{fc} , B^+ , B^- , and Δ values to check that the computational technique did not lead to anomalous results at odd combinations of parameters, and that the numbers used were physically reasonable.

The most important results from the theoretical studies are summarized in Figs. 1 and 2. Figure 1 shows a series of calculated spectra for $\Delta = 80$ meV, and a core lifetime and instrumental broadening of 1.8 eV full width at half maximum (FWHM) as a function of the weight of f^0 , c_{f^0} ,² in the ground state. Note that the ratio of the intensity the transitions to $3d^9f^1$ and $3d^9f^2$ final states tracks c_{f^0} fairly well, but the ratio does not give c_{f^0} exactly. This will be illustrated with Fig. 2.

In principle, a numerical fit to the spectra could be done to separate the contributions of $i \rightarrow f^1$ and

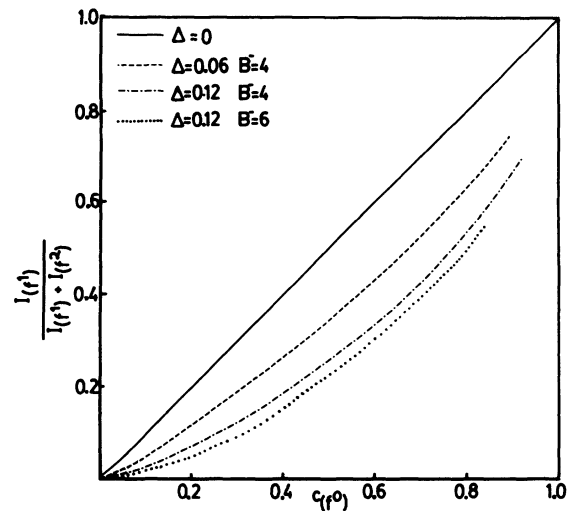


FIG. 2. Variation of the relative intensity of the $i \rightarrow f^1$ transition with the ground-state f^0 weight c_{f^0} . The curves shown were obtained by manual separation of calculated spectra, such as those in Fig. 1, and evaluation of the peak areas. For further details see text.

$i \rightarrow f^2$. However, such a fit should not use two simple Lorentzian peaks, but should include the multiplet effects and many-body tails. Such an effort would be out of proportion to its value, especially with the complexity of the $3d^94f^2$ multiplet. To discuss the important features, it is sufficient to estimate the peak areas by hand. Results for calculated XAS curves are shown in Fig. 2. The ratio of the $i \rightarrow f^1$ transition intensity divided by the total intensity is plotted as a function of c_{f^0} . While this ratio tracks c_{f^0} it is not equal to c_{f^0} , except when mixing of the f levels and the conduction states is nonexistent. Deviations are up to a factor of 2 in some cases with large hybridization ($\Delta \sim 120$ meV). We can vary the shape of the occupied part of the band by varying B^+ . Such a variation made essentially no difference to the curves in Fig. 2. Variation of B^- was also not relevant until B^- was of the order of the separation between the f^1 and f^2 peaks. In this range, final-state interaction distorts the spectra and changes the results of the deconvolution. For instance, for $\Delta = 120$ meV, changing B^- from 4 to 6 eV caused the deviation from proportionality to increase from $\sim 100\%$ to $\sim 120\%$ in the range $0 < c_{f^0} < 0.5$. Thus if I_{f^1}/I total is measured to be 0.2, c_{f^0} increases from 0.37 to 0.43 as B^- increases from 4 to 6 eV. We feel that such calculated deviations justify previously expressed caution with regard to derivation of the c_{f^1} from core-level spectra.^{23,25} The deviations are due to mixing of the

$\phi(f^0)$, $\phi(f^1)$, and $\phi(f^2)$ in the final state.³⁶ All other things being equal, the mixing of these wave functions is larger when their energy separation is small. Thus the effect is largest for $\phi(f^1)$ and $\phi(f^2)$ which are closest. However, because $I_{(f^1)}$ varies smoothly with $c_{(f^0)}$, it can be used to estimate $c_{(f^0)}$ if the hybridization Δ between f and conduction levels is known. We will take values for the hybridization from XPS studies.³²

EXPERIMENTAL

The intermetallic compounds used for this study were prepared by melting together the metals in the correct proportions under argon in a cold crucible. They were annealed *in vacuo*, if necessary, and were characterized by metallography and x-ray diffraction. The amount of secondary phases present was never more than 5%. The spectra were recorded by the photoyield method in a vacuum of 10^{-9} or better using samples scraped *in situ*. The only direct method of determining the contamination level in these experiments was by checking for the peaks due to oxide. No peaks were detected, but this is not a very sensitive test. However, the same scraping methods were used for XPS where contamination levels were always below 5 at. %.^{23,25,32} Note also that photoyield spectroscopy does not have the extreme surface sensitivity of XPS.

The observations were carried out on the background continuum emitted by the Anneau de Collisions d'Orsay (ACO) storage ring at Orsay, using a double-crystal monochromator equipped with beryl crystals. The resolution for this instrument is approximately 0.3 eV.³⁷ Checks were made on the light flux from the monochromator using Al, which has a flat absorption in the energy region of interest here. The only structure was due to a "glitch," or anomalous reflection of the crystals at 898 eV, for which we corrected using the Al reference. The energy scale was calibrated using the Ni $2p_{3/2}$, Cu $2p_{3/2}$, and Mg $1s$ edges as the binding energies of these levels are well known,³⁸ and only in the case of Ni is a small correction necessary for the narrow density of unoccupied states.

RESULTS

The experimental curves for Ce itself are shown in Fig. 3. There are two main groups of peaks due to $3d_{3/2}$ - and $3d_{5/2}$ -like final states. The ratio of the two groups is not 2:3 because of the effect of intermediate coupling.²⁹ We did find small changes in the relative intensities of these two peaks due to drift in the synchrotron radiation intensity (up to $\sim 10\%$). Structure due to the d^9f^2 multiplet splitting can be clearly observed in the data and matches

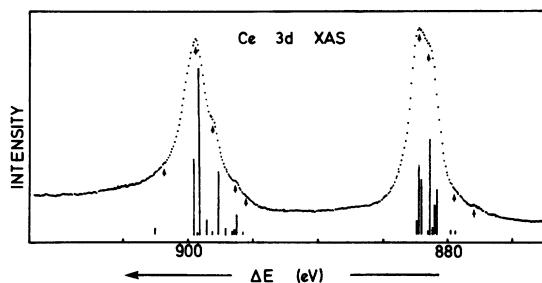


FIG. 3. $3d$ XAS spectrum of Ce showing the multiplet structure.

fairly well the spectrum calculated by Bonnelle *et al.*²⁹ In the pure Ce spectrum there is no obvious peak due to $i \rightarrow f^1$ transitions although the background does rise on the high-energy side of the main peaks. If peaks or shoulders are present in the region 5 eV to the high-energy side of the main peaks, then these have less than 2% of the main peak intensity, which, in combination with Fig. 2, would suggest that $c_{(f^0)}$ is below 0.06.

The small step in the background on the high-energy side of both the $3d_{3/2}$ and $3d_{5/2}$ peaks of Ce in Fig. 3 does present some problems. A similar effect was found for the La $3d_{3/2}$ peak and has been attributed to $3d \rightarrow$ continuum transitions³⁹ although there are some differences of opinion about its origin and the role of Fano-type effects.⁴⁰ In La no such step in the background is found for the La $3d_{5/2}$ peak, and the origin of the step at the Ce $3d_{5/2}$ peak puzzles us. It may be due to the continuum of Ce conduction states. It is important to note that the step is not constant, but is larger in compounds in which the $i \rightarrow f^1$ transition is observed, as illustrated in Fig. 4 for CeNi₅. Whatever its precise physical

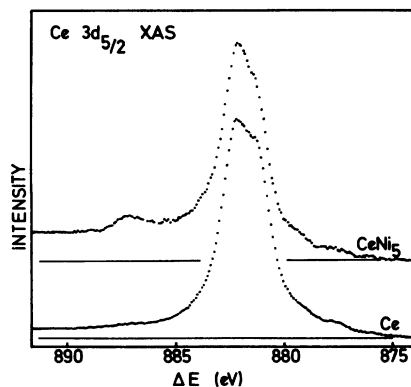


FIG. 4. $3d_{5/2}$ XAS spectra of Ce and CeNi₅. The spectra have been normalized to the main peak height. Note that the increase in background on the high-energy side of the main peaks changes.

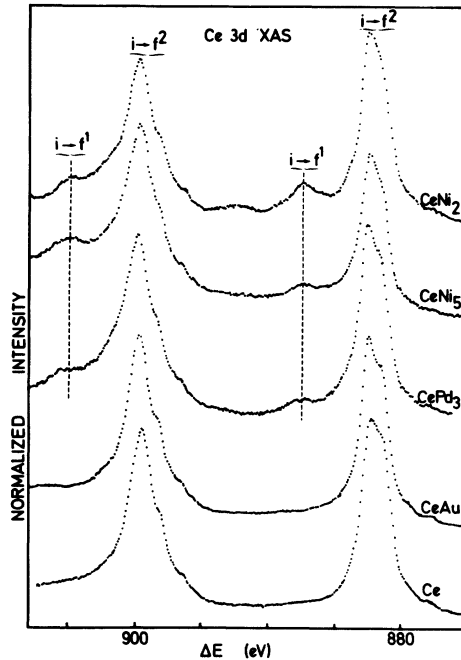


FIG. 5. 3d XAS spectra of Ce and some of its intermetallic compounds.

origin, this step in the background is a nuisance here because it makes it more difficult to extract quantitative information on the relative intensity of the $i \rightarrow 4f^1$ peak. It is always possible that a disproportionately high part of $i \rightarrow 4f^1$ oscillator strength goes into the long background. In the present case we can only extrapolate a linearly increasing background from ~ 885 to ~ 870 eV (or 895 – 910 eV for the $3d_{3/2}$ peaks) and subtract this before separating the peaks.

In Fig. 5 the Ce 3d XAS spectra of Ce, CeAu, CePd₃, CeNi₅, and CeNi₂ are compared. In the latter, three compounds' definite peaks due to transitions from the ground state to f^1 final states can be observed. Such peaks were not found in Ce₃Pd₅, CePd, and CeSn₃ which gave spectra very similar to that of Ce. It is worth noting that when $i \rightarrow f^1$ peaks were observed in XAS, $i \rightarrow f^0$ peaks were also found in XPS, and when the $i \rightarrow f^1$ peaks were absent in XAS, $i \rightarrow f^0$ peaks were not found in XPS, i.e., the spectroscopies yield compatible indications about whether the ground-state f^0 contribution is important or not. The same applies for bremsstrahlung isochromat spectroscopy.^{11,41}

In Table I we list the relative intensities of the $i \rightarrow f^1$ XAS peaks for the compounds studied. Also given are the values of $c_{(f^0)}$ obtained using Fig. 2 and the Δ values taken from Ref. 36.

TABLE I. Parameters relating to the ground-state weight of f^0 , $c_{(f^0)}$, as determined from 3d XAS.

Compound	$\frac{i \rightarrow f^1}{\text{total}}$	$c_{(f^0)}$	Δ from
			XPS, in meV)
Ce	~ 0.02	~ 0.04	30
CeSn ₃	< 0.02	< 0.04	50
CeAu	< 0.02	< 0.04	25
CePd	< 0.02	< 0.06	90
Ce ₃ Pd ₅	< 0.02	< 0.08	120
CePd ₃	0.06	~ 0.2	150
CeNi ₂	0.11	~ 0.22	100
CeNi ₅	0.08	~ 0.18	70

DISCUSSION

Over the past 30 years the model for Ce and its compounds that became most widely accepted was one in which the Ce 4f level was narrow (~ 10 meV) and in which the f count varied between 0 and 1 depending on the chemical environment of the Ce atoms, i.e., the 4f electron could be "promoted" to the conduction states. It was thought that the f count in CePd₃ was 0.6.³ On the basis of their magnetic properties, CeNi₂ and CeNi₅ were thought to have f counts near to zero.² Over the last decade or more this model has become increasingly controversial (see, e.g., Ref. 42) and in the last 2–3 years there has been increasing evidence from valence-band^{7–14} and core-level photoemission^{20,36} that the f levels must be broader than 10 meV. It was also felt on the basis of the core-level XPS spectra²³ and resonance photoemission studies of the f levels^{7–14} that the f count did not vary so strongly as previously thought and that Kondo-type effects might play a role in some of the properties of Ce compounds.⁴³

In this work we have shown that with the Gunnarsson-Schönhammer model XAS spectra of the 3d levels are consistent with a rather small variation of f count in all the Ce alloys studied. The values for $c_{(f^0)}$ in Table I are all below 0.2. If we make an allowance for the small mixing of f^2 character into the ground state then the f -level count determined by XAS is above 0.85 in all the compounds studied. Comparison with the systematics proposed for intermetallic compounds in the promotional model lead us to believe that if low $c_{(f^0)}$ are found in CeNi₂ and CeNi₅, then the weight of f^0 , $c_{(f^0)}$ in the ground state is low in all intermetallic compounds of Ce.

The question that must immediately be asked is how reliable are the conclusions from XAS at the 3d

edge. The possible inaccuracies arise from two sources. Firstly, there are errors that arise due to inaccuracy of the experimental peak separations or of the parameters determined within the computational scheme from XPS. Certainly there is some uncertainty in the values used for the parameters as well as in the peak separations and background effects. However, we certainly do not think that the $c_{(f^0)}$ values given in Table I could be increased by more than a factor of 2 and still be compatible with the observed spectrum and the model used.⁴⁴

Secondly, the other possible source of errors is in inadequacies of the model used. It is a model and does employ certain assumptions. However, the parameters derived under these assumptions are physically reasonable and can explain, not only the XAS results shown here, but also core-level XPS and valence-band photoemission data.⁴⁵ It may be that a model can be created which explains the XAS spectra observed here and does not require the high f counts we suggest. However, in our opinion such a model would have to include even stronger deviations from the old promotional model with narrow f levels ($W < 10$ meV) and large variations of f count.

CONCLUDING REMARKS

We have shown here that the Ce XAS spectra in the $3d$ edges are compatible with a model for Ce in-

termetallic compounds that includes larger f -level widths than previously assumed and larger f counts. The importance of these studies was that they provided a check on the conclusions derived from XPS core-level and valence-band photoemission studies. In assessing the potential of such XAS studies we note that the f count n_f and width Δ can be better assessed from core-level XPS studies. In XPS, $c_{(f^0)}$ is determined from the $i \rightarrow f^0$ peak intensity and Δ can be fixed almost independently from the $i \rightarrow f^2$ peaks. On the other hand, XAS does not have the extreme surface sensitivity of XPS and may be more suitable for certain experiments, such as temperature-dependent studies. Our work indicates that the $3d$ edges can be studied with sufficient resolution and signal-to-noise ratios to make such investigations feasible.

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