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Ce valence variation in intermetallic alloys: L_{III} absorption spectroscopy results

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L_{III} absorption spectroscopy measurements, using synchrotron radiation on the $\mathrm{Ce}_{1-x}R_x\mathrm{Pd}_3$, $R=\mathrm{La}^{3+}$, Y^{3+}, Th^{4+}, and U and the $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$ alloy systems are presented. The Ce valence variation from the L_{III} spectra analysis is correlated with the lattice-parameter variations in the alloys. The roles of the volume and valence of the substitutes in determining the Ce valence state are discussed. The results are discussed in terms of hybridization and current electronic theory.

INTRODUCTION

The technique of L_{III} absorption spectroscopy is playing an important, current role in the shaping of our understanding of valence mixing in rare-earth materials.[1-5] This role is based upon the rapid time scale for the x-ray absorption (relative to the intervalence tunneling time), and upon the well-resolved shift in the $2p_{3/2}$ (L_{III}) absorption threshold for different $4f$ occupation numbers.[1-4] Analysis of L_{III} absorption measurements in terms of a superposition of two absorption thresholds provides a direct, microscopic and relatively rapid method of comparing the valence states of rare-earth atoms in drastically different crystal structures. Since crystal-volume-based and magnetic-susceptibility-based estimates of valence already exist in a tremendous variety of unstable valence systems[2,3,6] it is both possible and important to mutually calibrate these estimates with L_{III}-based valence estimates. Whereas the results of such comparisons for the most mixed-valent materials have shown at least qualitative agreement,[2] Ce compounds have uniformly shown profound discrepancies between bulk-property-based and L_{III}-based valence estimates.[1,4,5] Bauchspiess *et al.*[1] investigated a wide range of Ce compounds and found the L_{III}-based valence estimates (V_3) to vary between 3.0 and about 3.3 even though the bulk-property based valence estimates (V_B) varied between 3.0 and 4.0. More recently Parks *et al.*[4] have shown a linear relation between V_3 and V_B with $3.0<V_3<3.21$ and $3.0<V_B<4.0$ in the $\mathrm{Ce(Ag,Pd)_3}$ and $\mathrm{Ce(Pd,Rh)_3}$ systems.[7] Here the disparity between the saturated L_{III} valence estimate of about 3.3 by Bauchspiess *et al.*[1] and 3.21 in Ref. 4 is due to the different functional forms and fitting procedures used in absorption-spectra analysis.

In this paper we extend the comparison of the L_{III}-derived valence estimate to crystal-volume-inferred valence changes in a set of Ce intermetallic compounds. In view of the above-cited sensitivity of V_3 to fitting procedure, we review our L_{III}-data-fitting procedure by discussing results on the compounds $\mathrm{CeAl_2}$ (3+ by volume) and $\mathrm{CeCo_5}$ (close to 4+ by volume). We then discuss the response of the Ce valence in $\mathrm{CePd_3}$ to Y^{3+}, La^{3+}, and Th^{4+}, and U substitution on the Ce sublattice. The relative role of the valence and effective volume of the substitute will be clearly evident in our results. Finally we will discuss the $\mathrm{CeAl_2}$ system and show that only a very small but measurable Ce valence change is associated with its chemical-pressure-induced (Sc-substitution-driven) volume collapse.

FITTING PROCEDURE: $\mathrm{CeAl_2}$ AND $\mathrm{CeCo_5}$

The photon-induced transition from a core state to a continuum involves a rounded step function usually represented by an arctan function.[8] In the case of L_{III} absorption in rare earths the vestiges of the atomiclike $2p_{3/2}\rightarrow 5d$ transition yields a Lorentzian feature just above the onset of the continuum absorption. In Fig. 1 we show our L_{III} absorption data for $\mathrm{CeAl_2}$ (background subtracted) along with our fit to this data. The separate Lorentzian and arctan features used in the fit are also

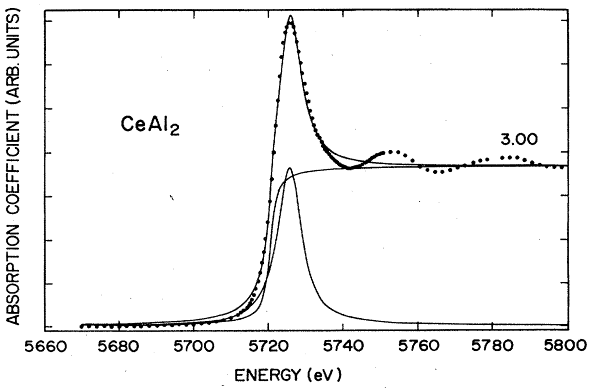

FIG. 1. L_{III} absorption threshold for trivalent $\mathrm{CeAl_2}$. The points are the data and the solid line passing close to the data is the theoretical fit. The functional form used to fit the data is the superposition of an arctangent step with a Lorentzian (see text) both of which are also shown as solid lines in the figure.

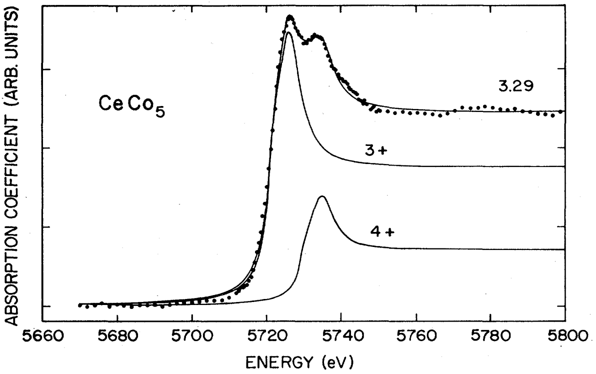

FIG. 2. L_{III} absorption threshold of $CeCo_5$, data (circles) and theoretical fit (solid line). The separate 3+ and 4+ absorption thresholds used to fit the data are also shown. In $CeCo_5$ our L_{III}-derived valence estimate is 3.29.

shown. The oscillation of the data about the fit at energies greater than 5740 eV is due to our neglect of the effect of electron backscattering from near neighbors on the extended x-ray absorption fine structure (EXAFS).[8] Such neglect of the EXAFS oscillations is conventional in L_{III} valence estimates.

Substantial Co-induced charge transfer mandates a valence of Ce in $CeCo_5$ which is near or at its maximum possible value (i.e., based on volume, one would assign the state Ce^{4+}). The L_{III} absorption spectrum of $CeCo_5$ is shown in Fig. 2. The theoretical fit to the data (the solid line passing close to the data), is comprised of a 3+ edge (peaking near 5725 eV) and a 4+ edge (peaking near 5735 eV). The relative intensities of the 3+ and 4+ edges in $CeCo_5$ yield a valence of 3.29 ± 0.01 for our saturated, maximum L_{III} valence within our fitting procedure. The errors on the fitted valence are statistical and are much smaller than the disparities arising from the choice of the functional fitting form.

$CePd_3$-BASED ALLOYS

The compound $CePd_3$ is one of the more extensively studied mixed-valence Ce compounds and has been assigned the valence of about 3.5 based on lattice volume estimates.[7,9] Gambke *et al.*[10] have studied the lattice parameters of $CePd_3$-based alloys in which trivalent atoms ($R=$La, Y, and Sc) have been substituted for Ce. They have reported that Ce is driven into its saturated valence state for $x=0.4$ in these $Ce_{1-x}R_xPd_3$ alloys. Gambke *et al.*[10] argue that (1) electronegativity drives rare-earth sublattice to Pd d band charge transfer thereby inducing a Ce valence greater than 3.0 in $CePd_3$; (2) R^{3+} substitution reduces the numbers of Ce atoms and therefore, the required charge transfer from each remaining Ce atom must increase with x in $Ce_{1-x}R_xPd_3$ alloys. Within this argument any trivalent substitute R should be equally effective in increasing the Ce valence. This argument explained the available lattice constant data of Gambke *et al.*, however, there is no mechanism in this argument to produce a saturated Ce valence less than 4 as one further dilutes the Ce ions (higher x).[4] Current theories of bonding in metals suggest that the more localized valence electrons bond by wave-function deformation.[11-13] This spatial deformation is driven by the electronegativity difference of the constituent atoms and results in wave-function spillover to adjacent ion cells. The saturation valence state for cerium can be identified with the state where the f electrons are fully hybridized and the L_{III} valence is a projection of f^0 and f^1 components of the deformed f wave function. The details associated with Ce valence variation are a matter of current interest. One theory that would lead to a saturation L_{III} valence less than 4 is the bistable $4f$-state model.[14] The points made by Gambke *et al.* (see above) are still valid if we agree that the charge transfer is by wave-function deformation (as opposed to f-electron promotion).

In Figs. 3 and 4 we show the L_{III} spectra of $CePd_3$ along with some Y- and La-substituted alloys. Also shown in these figures (as insets) are the lattice-parameter variations from Gambke *et al.*[10] from Croft and Levine,[15] and from Rao *et al.*[16] in these alloys. The lattice-parameter results on the $Ce_{1-x}Y_xPd_3$ system display a kink near $x=0.4$ (Fig. 3, inset), which Gambke *et al.*[10] ascribed to the onset of the saturated valence state for $x>0.4$. Referring to our L_{III} results for $CePd_3$ and $Ce_{1-x}Y_xPd_3$ (Fig. 3), the anticipated increased charge transfer is clear both from inspection of the spectra and from our fit results ($V_3=3.17$ and $V_3=3.29$, respectively). The smaller L_{III}-based valence estimates relative to bulk-property valence estimates are consistent with the trend pointed out in the Introduction. The fact that 40% Y substitution has not yet driven V_B to its maximum saturation value suggests that a more subtle volume effect in the $x>0.4$ region may also be occurring.

Considering the top two L_{III} spectra in Fig. 4 we see

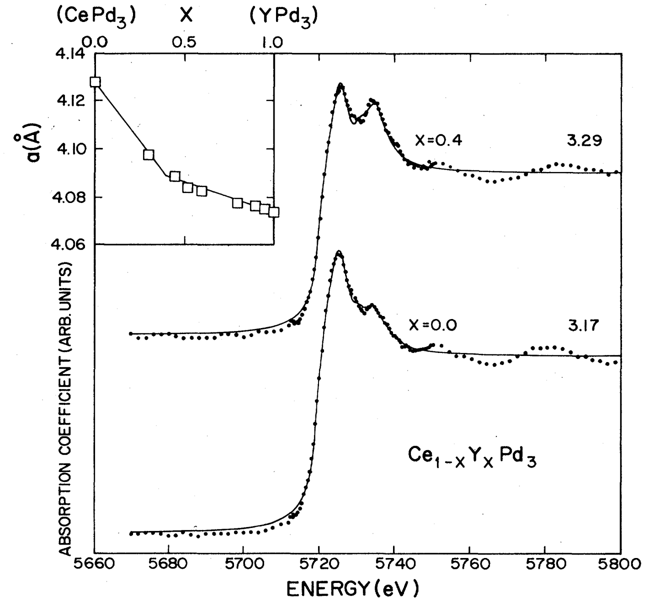

FIG. 3. L_{III} absorption spectra for $CePd_3$ and $Ce_{1-x}Y_xPd_3$. Inset is the lattice parameter vs composition variation in the $Ce_{1-x}Y_xPd_3$ series (from Ref. 10). Note the increase in Ce valence from 3.17 to 3.23 in correlation with the anomalous volume contraction with 40% Y substitution.

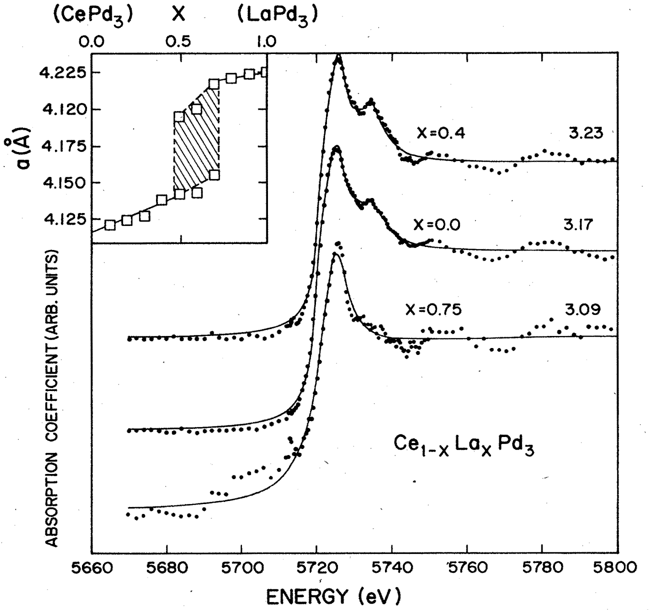

FIG. 4. L_{III} absorption spectra for $Ce_{1-x}La_xPd_3$, $x=0.4$ and 0.5 and $CePd_3$. Inset is the lattice parameter variation in the $Ce_{1-x}La_xPd_3$ system (from Refs. 10 and 15). The shaded region of the inset represents a two-phase region. Note the increase in the L_{III}-derived Ce valence (V_3) from 3.17 at $x=0$ to 3.23 at $x=0.4$. Note also the jump decrease in V_3 to 3.09 at $x=0.75$ in correlation with the lattice-parameter jump increase.

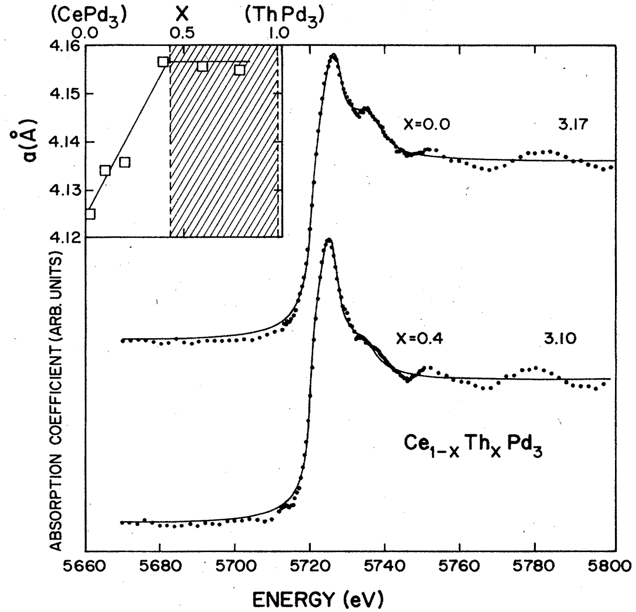

FIG. 5. L_{III} absorption spectra of $CePd_3$ and $Ce_{1-x}Th_xPd_3$. Inset is the lattice parameter (of the cubic phase) x in the $Ce_{1-x}Th_xPd_3$ system. The shaded area is a two-phase cubic hexagonal transition region. Note the decrease in Ce valence ($V_3=3.17$ at $x=0$ and $V_3=3.10$ at $x=0.4$) with Th substitution correlating with the lattice-parameter increase.

that a similar valence increase ($V_3=3.17$ for $CePd_3$ to $V_3=3.23$ for $Ce_{0.6}La_{0.4}Pd_3$) occurs for La^{3+} substitution. The degree of the charge transfer is substantially less, however, for 40% La substitution than for 40% Y substitution. This indicates that the higher volume of the La (relative to Y) must also play an important role in determining the Ce valence state in such $CePd_3$-based systems.

The lattice-parameter results for the $Ce_{1-x}La_xPd_3$ system (see Fig. 3, inset) indicates an isostructural volume expansion between $x=0.5$ and 0.75 along with an intervening two-phase behavior (hatched area in inset of Fig. 4). It is natural to associate a decrease in the Ce valence with this volume expansion. Indeed transport measurements in our laboratory and elsewhere have indicated strongly mixed-valence behavior for $x<0.5$, but Kondo-like close to Ce^{3+} behavior for $x>0.75$.[15] In spite of a decreased signal-to-noise ratio (due to the Ce dilution), the hardening of the Ce valence toward 3+ is clear in the $x=0.75$ spectra and the fitted valence of $V_3=3.09$ is obtained for $x=0.75$.

From the above it is clear that L_{III} absorption spectroscopy microscopically confirms the qualitative bulk-property-determined valence variation trends in these $CePd_3$ alloys. Quantitatively, however, the L_{III} measurements provide much more detailed information and suggest a different interpretation of some of the lattice-parameter-only—based conclusions. Specifically, we observe that the postulated Pd-electronegativity-driven (Ce f level)-to-(Pd d-band) admixture is operative but that lattice volume effects can play an enhancing or mitigating role in the Ce-valence increase. With these refined conclusions, we wished to address the roles of Ce-to-Pd admixture and Pd d band filling by the much more drastic substitution of Th^{4+} for Ce. The effect on Ce valence of the smaller volume of Th should be overwhelmed by the much higher valence of Th and one might expect a rapid hardening of the Ce valence toward 3+ upon Th substitution.

In Fig. 5 we show the L_{III} spectra of $Ce_{0.6}Th_{0.4}Pd_3$ and for comparison that of $CePd_3$ The substantial quenching of the 4+ peak in the spectra and the valence estimate of $V_3=3.10$ in the thorinated compound confirm the band-filling-type effect of the Th^{4+} substitution. The initial increase in the lattice parameter, with increasing x, in this alloy also supports the above conclusion, since a stable Ce radius in this alloy would have lead to a lattice-parameter decrease upon substitution of the smaller Th atoms. The change of crystal structure for $x>0.4$ prevents pursuing this alloy series to higher x. For $Ce_{0.6}U_{0.4}Pd_3$ a similar behavior is found with L_{III} valence $V_3=3.09$ and initial increase in lattice constant upon U substitution in this system.

$CePd_3$ ALLOY VALENCE: RPd_3 BAND PARAMETER COMPARISON

Finally, we note that there is a correlation between Pd d-band position relative to E_F [as determined from x-ray photoelectron spectroscopy (XPS) data of Fuggle *et al.*[17,18]] and our L_{III} valence estimates. In RPd_3 compounds, those with E_F further above the Pd d band edge than $CePd_3$ tend to lower the Ce valence in $Ce_{1-x}R_xPd_3$

TABLE I. Comparison of $R\mathrm{Pd}_3$ band parameters from XPS data with $\mathrm{Ce}_{0.6}R_{0.4}\mathrm{Pd}_3$ L_{III} valence. Note the correlation of L_{III} valence with Pd d band edge.

Constituent X in the compound $\mathrm{Ce}_{0.6}X_{0.4}\mathrm{Pd}_3$	$X\mathrm{Pd}_3$ Pd d band centroid C	$X\mathrm{Pd}_3$ Pd d band half-width HW	$X\mathrm{Pd}_3$ Pd d band edge $C+\mathrm{HW}$	$\mathrm{Ce}_{0.6}X_{0.4}\mathrm{Pd}_3$
U	-3.60	2.60	-1.00	3.09
Th	-3.50	2.60	-0.90	3.10
Ce	-3.10	2.75	-0.35	3.17
La	-2.50	2.55	$+0.05$	3.23
Y	-2.60	2.70	$+0.10$	3.29

alloys. Table I illustrates this point. The Pd-band centroids (C) and Pd d band half widths (HW) are from Fuggle *et al.*[17]

Interpretation of the L_{III} valence versus Pd d band-edge correlation follows below. Since the Pd d band and Ce f levels are fairly localized we consider them as fixed in energy.[11]

E_F varies due to band filling in the case of Th and U substitution and E_F varies due to chemical pressure effects in the case of Y and La substitution. Upon band filling with Th and U substitution there are two nearly equivalent effects: The excess electrons satisfy the Pd d band electronegativity requirement, and E_F is raised as in a noninteracting Fermi gas due to the greater conduction electron count. It is the first effect which frees Ce f electrons from that role thereby leading to a lower Ce valence with these substitutes.

In pure CePd_3 the Pd d band lies 0.35 eV below E_F. As La or Y is substituted for Ce, the excess partial f electron from the Ce ions in the conduction band is removed, and E_F falls due to a lower conduction electron count.

The smaller YPd_3 lattice constant compared to LaPd_3 causes a wider Pd d band in the Y substitute and therefore the top of the Pd d band is further above E_F in the Y substitute (0.1 eV above E_F as opposed to 0.05 eV above in the La substitute). In our argument a higher Pd d band top implies less satisfaction of the Pd d band electronegativity requirements. This unsatisfied requirement is felt by the cerium atoms, inducing a greater degree of charge transfer. For this reason the Y substitute has higher Ce valence than the La substitute.

CeAl_2 AND $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$

The compound CeAl_2 is a widely studied close-to-trivalent, Ce system.[3,15,19] With an antiferromagnetic ordering temperature of 3.85 K and an estimated Kondo temperature of about 5 K, it has been discussed extensively as a concentrated Kondo compound.[3,15,19] The onset of a volume-collapsed nonmagnetic state above about 7% volume compression has been demonstrated both by high-pressure experiments on CeAl_2 and by work on the chemically compressed $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$ system.[15,20–23] In order to prove the degree of valence change associated with this transition in CeAl_2 we have performed L_{III} absorption spectroscopy on both CeAl_2 and on $x=0.7$ collapsed-volume alloy.

In Fig. 6(a) we present the L_{III} spectra for CeAl_2 (solid line) and for $\mathrm{Ce}_{0.3}\mathrm{Sc}_{0.7}\mathrm{Al}_2$ (circles), both normalized to the peak of their absorption. The increase in the step height relative to the peak and a small bump in the 5735-eV energy range (the 4+ white line position) indicate only a small increae in the 4+ contribution to the spectrum in the $\mathrm{Ce}_{0.3}\mathrm{Sc}_{0.7}\mathrm{Al}_2$ sample. The small degree of the 4+ edge intensity compared to the nearby 3+ edge and EXAFS oscillations makes a direct quantitative fit to the Sc-substituted spectra nearly impossible. To help extract

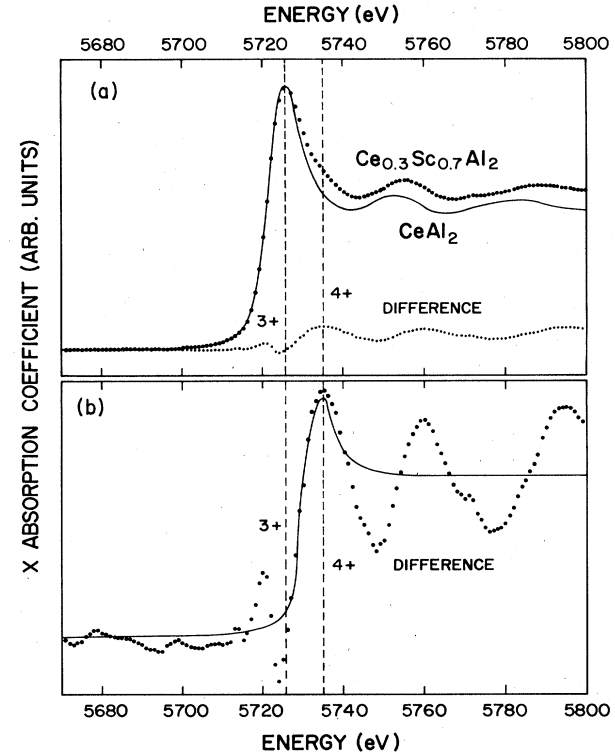

FIG. 6. (a) L_{III} abosrption spectra of CeAl_2 (solid line) and $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$ (circles) both normalized to the Ce white-line peak. Note the small shoulder near the 4+ threshold position and the smaller white line to step height ratio for the Sc alloy spectrum. Also shown (on the same vertical scale) is the difference spectrum obtained by subtracting the CeAl_2 data from the $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$ data. (b) Difference spectra from (a) displayed on a much expanded scale. The solid line is a theoretical fit of the difference spectra to Ce L_{III} absorption threshold. The Ce valence of $\mathrm{Ce}_{1-x}\mathrm{Sc}_x\mathrm{Al}_2$ determined by this fit was 3.07.

the 4+ edge we have subtracted the data of the $CeAl_2$ L_{III} spectra from the L_{III} spectra data for $Ce_{0.3}Sc_{0.7}Al_2$ where both sets of data are normalized to their white line peaks. The difference spectra are also shown in Fig. 6(a), on the same scale as the individual spectra. The difference spectra are shown in Fig. 6(b) on a much expanded scale.

Formation of the difference spectra essentially removes the very strong 3+ edge structure, and partially reduces the EXAFS oscillations. Referring to Fig. 6(b), one can see that for the difference spectra the 4+ edge white line is larger than the structure in the EXAFS region of the spectra. The derivative-shaped structure near 5720 eV is caused by a small difference in the 3+ edge line shapes between $CeAl_2$ and $Ce_{0.3}Sc_{0.7}Al_2$ and makes little or no contribution to the analysis of the 4+ edge.

Fitting the difference spectra with a single 4+ edge yields the solid line in Fig. 6(b). Fixing the 4+ edge amplitude determined from the difference spectrum and varying the 3+ edge to fit the total $Ce_{0.3}Sc_{0.7}Al_2$ spectra, one finds a valence $V = 3.07$. Thus while a *definite* L_{III}-determined increase in valence appears to be associated with the volume collapse in the $(Ce,Sc)Al_2$ system, the degree of valence increase is extremely small. We attribute this weak valence variation to the lack of states with which the f electrons can hybridize.

SUMMARY AND CONCLUSIONS

We have presented L_{III} absorption results on a number of Ce intermetallic alloys and have verified that the lattice parameter anomalies in these alloys are associated with changes in the Ce valence. Moreover the precision and sensitivity of the L_{III} results allow refinement of "lattice-parameter-only"–based conclusions regarding valence variation in these Ce alloys.

Specifically regarding the $Ce_{1-x}R_xPd_3$ alloys: (i) The Ce-valence increase with x for $x < 0.4$, $R = La^{3+}$, and Y^{3+}, as expected from electronegativity arguments is confirmed; (ii) The secondary but measurable role (for $x < 0.4$) of the effective volume of the substitutes $R = La^{3+}$ and Y^{3+} on the Ce alloy valence is established; and (iii) the dramatic hardening of the Ce valence toward Ce^{3+} for $x > 0.75$ in the volume-expanded $Ce_{0.25}La_{0.75}Pd_3$ alloy is established and the rapid hardening of the Ce valence toward Ce^{3+} with band filling for $R = Th^{4+}$ and U substitution is established. XPS d-band energy centroids of RPd_3 substitutes are found to have a correlation with L_{III} valence. This correlation is explainable in terms of band filling. Regarding the $Ce_{1-x}Sc_xAl_2$ system, the volume collapse for $x > 0.5$ is established to involve an increase in Ce valence but an increase so small that a more sophisticated method is required to analyze the L_{III} spectra. The degree of L_{III} valence variation upon chemical environment changes seems to correlate with the availability of conduction states with which the f levels can hybridize. In $Ce_{1-x}Sc_xAl_2$ in which the Al-sublattice conduction-band components are p-like with a low density of states, the rather extreme substitution at $x = 0.7$ along with a 15% volume reduction[22] with respect to $CeAl_2$ produces only a L_{III} valence change of 0.07 electrons. In $CePd_3$, however, there is a high density of states d band due to Pd $4d$ states,[13] and the valence is varied rather easily by chemical environment effects. Thus it appears that L_{III} absorption spectroscopy provides a valuable tool both to confirm and to extend significantly other bulk-property-based conclusions on mixed-valence materials.

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