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Chemical environment and Ce valence: Global trends in transition-metal compounds

R. A. Neifeld and M. Croft
Physics Department, Rutgers University, Piscataway, New Jersey 08854

T. Mihalisin
Physics Department, Temple University, Philadelphia, Pennsylvania 19122

C. U. Segre and M. Madigan
Physics Department, Illinois Institute of Technology, Chicago, Illinois 60616

M. S. Torikachvili and M. B. Maple
Physics Department, University of California, San Diego, La Jolla, California 92093

L. E. DeLong
Physics Department and Astronomy Department, University of Kentucky,
Lexington, Kentucky 40506

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Results of L_{III} absorption spectroscopy measurements on a wide range of Ce–transition-metal (T) compounds are presented and Ce valence-state estimates are made. We are able to identify extremely regular trends in the response of the Ce valence and Ce-T hybridization strength to systematic variations in the solid-state chemical environment. Our work facilitates identification of the specific elements in the T-metal electronic structure which drive the Ce valence-state change.

The last $4f$ electron in Ce, Sm, Eu, Tm, and Yb is energetically weakly bound despite the fact that it resides deep within the core of the atom. The solid-state chemical environment of these atoms dictates whether this electron will remain bound within the core, join the spatially extended valence electrons, or reside partially in both.[1-5] In this last case, the atom is said to be in a "mixed-valent" (MV) state with the partial charge transfer out of the $4f$ shell being characterized by the atom's nonintegral "valence state." We present here quantitative results on the systematic response of the Ce valence to a wide but systematic variation in chemical environment. Specifically, we present results on some sixty $3d$, $4d$, and $5d$ transition-metal (T) compounds of the form $\mathrm{Ce}T_x$, $\mathrm{Ce}T_2\mathrm{Si}_2$, and $\mathrm{Ce}T_2\mathrm{Ge}_2$. Our results allow certain inferences to be drawn regarding the Ce valence-state response to specific T-metal-induced changes in electronic structure. Indeed, our work suggests for the first time that the valence state of MV atoms may in some cases be useful probes of such electronic structure changes.

L_{III} absorption spectroscopy has been applied successfully for valence estimation in a wide range of MV materials.[6-9] To illustrate the technique, shown in Fig. 1 (bottom) are the separate Ce^{3+} and Ce^{4+} contributions, which we have superimposed to fit the L_{III} edge of $\mathrm{Ce_2Co_{17}}$. The integral valent edges are each modeled by the sum of a Lorentzian "white line" (WL) representing transitions from the Ce $3p_{3/2}$ level into empty Ce $5d$ states above the Fermi energy plus an arctangent step representing transitions with final states in the continuum. The L_{III} valence v is estimated by the relative fraction of each integral valent edge feature required to fit the spectra, i.e., $v=(3A_3+4A_4)/(A_3+A_4)$, where A_n is the area of the Lorentzian white line associated with the nth valence state. The details of our data analysis

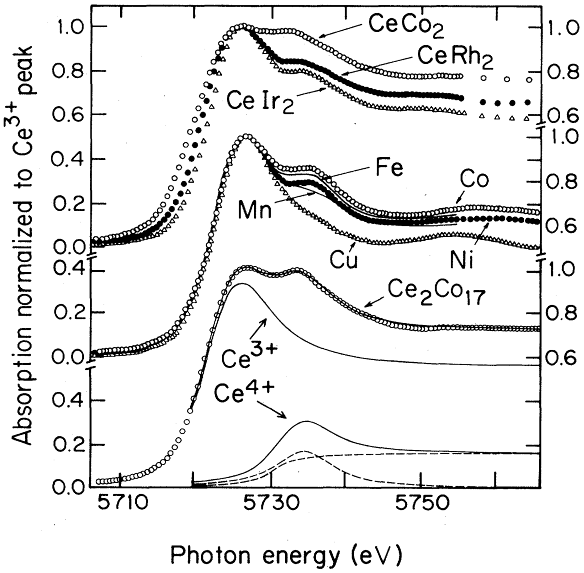

FIG. 1. L_{III} absorption spectra, all normalized to the Ce^{3+} peak. The top set of spectra, all on the same scale, are for $\mathrm{CeCo_2}$, $\mathrm{CeRh_2}$, and $\mathrm{CeIr_2}$, all of which have the $\mathrm{MgCu_2}$ structure. The middle set of spectra, are the $\mathrm{Ce}T_2\mathrm{Si}_2$ for $T=$ the $3d$ transition metals Cu (Δ), Ni (●), Co (○), and Fe and Mn (solid lines), all of which have the $\mathrm{ThCr_2Si_2}$ structure. The bottom spectrum is for $\mathrm{Ce_2Co_{17}}$ (○). Deconvolution of the $\mathrm{Ce_2Co_{17}}$ fit to the spectra is shown on the same scale. The separate Ce^{3+} and Ce^{4+} lines are shown. Below the Ce^{4+} feature are the spectrum's arctangent and Lorentzian components which comprise it (dotted lines).

methods will be discussed at length elsewhere.[8-10] It is important to emphasize that, despite the widespread use of the L_{III} technique, the random assortment of compounds studied and the differences between experimental groups in data analysis have previously precluded the correlation of these results into a coherent global chemical picture of the type developed in this paper. We have, moreover, pushed our investigation to lower d-count T-metal compounds than in previous L_{III} measurements.

The relationship between our L_{III} measurements and the lattice volume, magnetic susceptibility, and transport measurements often used to characterize Ce compounds is facilitated by identifying three ranges for v (the L_{III}-derived valence estimate): (1) The "Kondo" regime with $3.00 < v < 3.12$, in which materials show an interplay of magnetism and Kondo-effect-type spin-fluctuation phenomena, (2) the "saturation" regime with $3.26 < v < 3.35$, where local moment magnetism is absent and the Ce ion volume collapse has evidently achieved its fullest extent, and (3) the "intermediate" regime with $3.13 < v < 3.25$, where the presence of both valence states are reflected in the atomic volume and magnetic properties.

We assume that the value our L_{III} analysis yields for v directly reflects the Ce valence, although we do not assert that it is numerically equal to the chemical valence. The one-to-one (and nearly linear) relation between L_{III} valence estimates and traditional valence probes such as crystal volume (in Ce systems)[7] and Mössbauer isomer shift (in Eu systems)[9] provides good precedent for this assumption. Thus, while we believe that our results provide direct evidence regarding the relative degree of charge transfer out of core $4f$ states, we do not address the important questions of the absolute magnitude and character of this transfer. In the discussion below we have attempted to pick out some of the clearest chemical trends in the intermetallic series we have studied.

We wish to illustrate both the differences between L_{III} spectra (in an analysis-independent way) and the spectrum changes upon changing v or the $5d$-band width. Specifically, we will directly compare selected L_{III} spectra by superimposing them normalized to the height of the first (Ce^{3+}-related) absorption peak. The superimposed spectra of several compound series discussed below are shown in Fig. 1. Since increasing valence results in the transfer of spectral intensity from the first (normalization) peak to the higher-energy peak, the spectra of higher valence materials should lie uniformly above that of lower valence materials in such a superposition. Similarly, changes in the WL linewidths are highlighted by this superposition method.

The plots of the v variation in several compound series are shown in Figs. 2(a) and 2(b). First among the chemical trends in v we wish to note is the occurrence of a maximal value (v_m) as T is varied across a transition-metal row within a given chemical formula (e.g., CeT_2Si_2 or CeT_2). As can be seen in Figs. 2(a) and 2(b), v_m can fall in the "saturated" regime (as for $CeCo_2$, $CeCo_5$, $CeRh_3$), in the intermediate regime (as for $CeCo_2Si_2$), or in the Kondo regime (as for $CeCo_2Ge_2$ or $CeRu_2Si_2$). This trend is most apparent in the CeT_2Si_2 series for $T = 3d$ series. The superimposed spectra in Fig. 1 (middle) illustrates the increase of v as T varies from Cu to Ni to Co followed by a decrease in v from $T = $ Co to Fe to Mn. The CeT_2 series, with $T = $ Cu, $Ni_{1-x}Co_x$, Co, Fe, and $Fe_{1-x}Mn_x$ also clearly shows the occurrence of v_m [Fig. 2(a)]. The low valences of Ce in Sc, Y, and La further underscore the notion that a Ce valence decrease should occur for Ce-T materials as T varies from Co to Sc, from Ru to Y, and from Os to La. In identifying this heretofore unrecognized decrease in the Ce valence with decreasing T-metal electron count, our work motivates studies of MV Ce in a new class of materials with novel d-band electronic structure.

It should be noted that v_m occurs further to the left for T in the $4d$ and $5d$ rows than in the $3d$ row. In the $MgCu_2$ and $ThCr_2Si_2$ structure compounds, for example, v_m occurs near Co in the $3d$ row, but at Ru or further left in the periodic table for the $4d$ elements and at Os or further left in the periodic table for $5d$ elements. Similar effects are observed in the cohesive properties (e.g., boiling point, bond length, and work function) of the transition metals and their compounds.[11] These properties reflect cohesive and Fermi-energy variations due to an interplay of the T-metal d-band bandwidth (W), correlation energy (U), and crystalline-

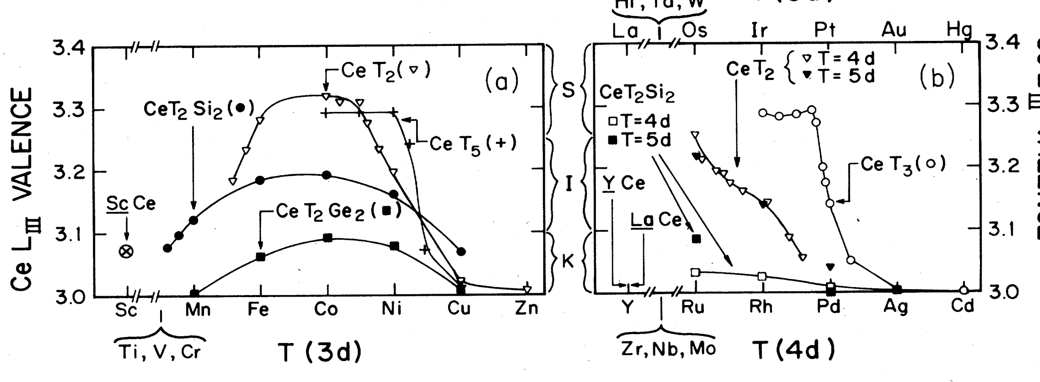

FIG. 2. L_{III} valence vs d-band metal. Three general regimes of valence are outlined highlighting the correspondence between V_L and known transport properties and lattice volume of compounds in each regime: (1) Kondo (K), (2) intermediate valent (I), and (3) saturated valent (S) (see text). Solid lines between data points are a guide to the eye. (a) L_{III} valence vs $3d$ transition-metal component for several compound series. Symbols for the series are CeT_2 (▽), CeT_2Si_2 (●), CeT_2Ge_2 (□), $Ce_{0.12}Sc_{0.88}$ (⊗), CeT_5 (+). (b) L_{III} valence vs $4d$ (bottom ordinant) or $5d$ (top ordinant) transition-metal component for several compound series. Symbols for the $T = 4d$ series are CeT_2 (▽), CeT_2Si_2 (□), CeT_3 (○), and for $T = 5d$, CeT_2 (▼), CeT_2Si_2 (■); valences of $Ce_{0.15}Y_{0.85}$ and $Ce_{0.17}La_{0.83}$ represented by arrows.

electric-field (CEF) energy.[12–14] In Table I we note the occurrence of maxima in the T-metal cohesive energies in various simplifying regimes of these competing energies. The three basic physical effects which go into Table I are (1) for $U \rightarrow 0$ electrons fill states without regard to spin, whereas for $U \rightarrow \infty$ all spin-up states fill first, (2) bonding (hybridization) energy is maximized when a band is one-half filled, and (3) the CEF yields a cohesive energy increasing when electrons are added to the lower CEF level.

We believe it is the T-metal contribution to the electronic structure of these Ce-T compounds which dominates the Ce valence trends and which causes the Ce valence state to track the T-metal cohesive properties. Referring to Table I, this interpretation suggests that the shifting of v_m from $n \sim 7$ in the $3d$ elements to $n \sim 6$ or less in the $4d$ and $5d$ elements reflects the loss of d-band correlation. It is also clear that the CEF and hybridization contributions to the lowering of the Fermi energy would both tend to drive the occurrence of v_m near the same general value of d-band filling (e.g., $n \sim 7$–8 for the former and $n \sim 7.5$ for the latter in the $3d$'s). The relative weight of these last two effects will vary from system to system depending on the density, crystal symmetry, and chemical bonding.

In Fig. 1 (top) we compare the L_{III} spectra of CeT_2 for $T =$ Co, Rh, and Ir. The large Ce valence decrease between CeCo$_2$ and CeRh$_2$ is again driven by the substantial loss of T-metal d-band correlation as discussed above. The smaller valence decrease between $T =$ Rh to $T =$ Ir is presumably related to the volume sensitivity of the Ce valence along with the volume increase on moving from Rh to Ir. Similar trends in Ce valence are repeated in the CeT_2Si$_2$ series as T is varied from $3d$ to $4d$ rows [compare the data in Figs. 2(a) and 2(b)]. The decrease in v between the CeT_2Si$_2$ and CeT_2Ge$_2$ series (with T in the $3d$'s) is presumably due to a similar volume coupling mechanism.

The data in Figs. 2(a) and 2(b) also suggest certain systematics in the v variation for binary intermetallics of the form CeT_x. To clarify this situation, we have determined v vs x results for known CeT_x intermetallics with $T = 3d$ elements. As expected for $T =$ Zn and Cu, increasing x stabilizes the integral valent $v = 3.00$ state. On the other hand, the trend with $T =$ Ni, Co, and Fe is to stabilize "saturated" regime values of v upon increasing x (e.g., for $T =$ Ni one finds $v = 3.03$, 3.06, 3.17, 3.27, 3.28, and 3.29 for $x = \frac{3}{7}$, 1, 2, 3, $\frac{7}{2}$, and 5, respectively); in the CeCo$_x$ series, $v = 3.08$, 3.32, 3.29, and 3.29 for $x = \frac{11}{24}$, 2, 5, and $\frac{17}{2}$, respectively; in the CeFe$_x$ series, $v = 3.27$, 3.28, for $x = 2$, $\frac{17}{2}$, respectively. The high v for CeCo$_2$ is related to the broad lines in the maximal valent Ce $3d$ binary compounds.

TABLE I. T-metal d-electron count (n) and element where a local maximum in the cohesive energy occurs in the cases of large and small correlation energy (U), zero crystalline-electric-field (CEF) splitting, finite and zero d-band width (W) and finite CEF splitting, with e_g and t_{2g} orbitals lowest in energy. Note we have applied the case of low correlation (low spin) to the $4d$ and $5d$ elements and that of high correlation (high spin) to the $3d$ elements. Note also that our results indicate that the Ce valence variation between Ce-T compounds will track the T-metal contributions to the compounds' cohesive energy.

	W $\sim$ 0 CEF present e_g lowest	W $\sim$ 0 CEF present t_{2g} lowest	$W \neq 0$ No CEF
$U \rightarrow 0$	$n = 4, \begin{cases} \text{Mo} \\ \text{W} \end{cases}$	$n = 6, \begin{cases} \text{Ru} \\ \text{Os} \end{cases}$	$n = 5, \begin{cases} \text{Tc} \\ \text{Re} \end{cases}$
$U \rightarrow \infty$	$n = \begin{cases} 2, \text{ Ti} \\ 7, \text{ Co} \end{cases}$	$n = \begin{cases} 3, \text{ V} \\ 8, \text{ Ni} \end{cases}$	$n = \begin{cases} 2.5, \text{ Ti—V} \\ 7.5, \text{ Ni—Co} \end{cases}$

Finally, we wish to note that Ce $5d$-band width information is contained in the WL linewidths of the L_{III} spectra. Although the experimental resolution, $2p$ hole lifetime, and the $5d$-band width all contribute to the WL linewidth, the former two contributions are essentially constant throughout all our spectra. Hence we associate variations in the WL linewidths with variations in the Ce $5d$ orbital width in a given chemical environment. This linewidth information also allows comparison of the chemical environment within and between compound series. Within a given compound series we observe an essentially uniform narrowing of the WL as T is varied down a column from the $3d$ to $4d$ to $5d$ rows (e.g., the linewidths of CeT_2Si$_2$ for $T =$ Cu, Ag, and Au are, respectively, 9.8, 9.2, and 8.3 eV). This narrowing trend is well illustrated by the CeT_2 spectra in the top of Fig. 1 as T varies from Co to Rh to Ir. Turning to between-compound comparisons, the WL's (hence Ce $5d$ hybridization widths) in the CeT_2Si$_2$ series and in the alloys of Ce in Sc, Y, and La appear 1–2 eV narrower than in the CeT_2 series for a given T. While the Ce $5d$-band width could be of interest in mixed-valent Ce systems, the Ce $4f$ hybridization is of course of much greater interest. Since both the $5d$ and $4f$ widths are strongly influenced by wave-function overlap with near-neighbor T-metal functions the $4f$ and $5d$ widths should roughly track on another (though the f hybridization is much smaller).[15] Thus the $5d$-width information gleaned from L_{III} studies could be of use in sorting out the role of the $4f$ width in mixed-valent Ce systems.

Our results enable one to begin to form a global picture of the response of the Ce $4f$ orbitals to a broad range of chemical environments in a quantitative manner. In doing so, a number of specific research goals are clearly identified: (1) development, from a solid theoretical basis, of the analysis of the near-edge x-ray absorption structure of mixed valence materials, (2) a theory of cohesion and f-electron bonding which can accurately predict and explain MV ion valence variation, (3) detailed and critical comparison of other spectroscopic, lattice, and thermal measurements to our L_{III} results over a similar broad chemical range, and (4) experimental work on new stable and metastable materials involving transition metals with d-band occupancy of 6 or less. Finally, our work supports the novel notion that the $4f$-level occupancy of mixed-valent atoms may prove to be a quantitative marker with which to probe the band structure of materials.

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[12] See J. Huhey, *Inorganic Chemistry* (Harper and Row, New York, 1983), Chap. 9.

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