PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983

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$L_{\rm III}$ x-ray absorption in the light rare earths: Ground-state versus final-state effects

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(Received 26 October 1982; revised manuscript received 7 February 1983)

X-ray $L_{\rm III}$ absorption-edge measurements have been performed on a number of mixed-valent Ce-based systems, along with their La- and Pr-based isomorphs. Contrary to several conjectures, the results imply that the ratio of the integrated intensities of the two edges observed in Ce-based systems is not altered appreciably by final-state effects and hence is a reflection of the $4f$ ground state.

Mixed-valent rare-earth systems exhibit a double edge in $L_{\rm III}$ x-ray absorption spectra (see, e.g., Ref. 1 and references cited therein). This reflects the relative strengths of the $4f^n$ and $4f^{n-1}$ components in the ground state. In the presence of a $4f$ hole, the $L_{\rm III}$ edge, which represents excitation of the $2p$ core level into the conduction band, is shifted by approximately 10 eV to higher binding energy. The ratio of the two intensities provides a relatively accurate determination of the mixed valence in Eu-, Sm-, Tm-, and Yb-based systems, the latter being well described by the promotional model of mixed valence, wherein the $4f$ electron is promoted to the conduction band in the $4f^{n-1}$ state.[1]

Recently, Bauchspiess *et al.*[2] reported the observations of a double edge in the $L_{\rm III}$ absorption edge of numerous Ce-based compounds which are thought to be tetravalent or nearly tetravalent on the basis of magnetic susceptibility and lattice-constant measurements, and hence should exhibit only a single edge. This observation adds to an ever expanding body of evidence that $4f$-unstable Ce-based systems cannot be described by the simple promotional model. Particularly compelling are valence-band photoemission experiments which fail to reveal a single $4f$ emission at E_F, as required by the promotional model,[1] in "mixed valent" cerium-based systems.[3,4] In addition, a variety of experiments suggest that there is a negligible change in the number of $4f$ electrons at the γ-α transition in cerium (e.g., positron annihilation,[5] Compton scattering,[6] neutron scattering,[7] and photoemission[3]).

The purpose of the present investigation was to establish if the double $L_{\rm III}$ edge feature observed in "mixed valent" and formally tetravalent Ce-based systems reflects solely the $4f$ ground-state configuration or, alternatively, if it is altered by final-state effects. Lengeler *et al.*[8] have conjectured that the higher-energy feature of the double edge observed in α cerium is due solely to the shakeup process

$$2p^*4f^15d^26s^2 \rightarrow 2p^*4f^05d^36s^2 \qquad (1)$$

(where $2p^*$ denotes a $2p$ hole), corresponding to an effective valence of 3.0 in the ground state (i.e., $f^1=1$). On the other hand, Bianconi *et al.*[9] have suggested that the ratio of the two edge features observed in CePd$_3$ is dramatically altered by the shakedown process

$$2p^*4f^05d^36s^2 \rightarrow 2p^*4f^15d^26s^2 \ , \qquad (2)$$

which would imply that the effective valence in the ground state is markedly larger than given by the ratio of the two edge features.

We have used the term "effective valence" instead of valence above, because of the failure of the promotional model to describe the $4f$ instability in Ce-based systems as discussed above. In the promotional model the term "valence" is well defined, viz., it is the conduction-electron count which is directly related to the $4f$ occupancy. However, the "effective valence" for Ce-based systems is a more ambiguous quantity, whose value depends on the property measured, e.g., lattice-constant measurements suggest a different effective valence than x-ray photoemission (XPS) or x-ray absorption measurements.[1]

Shakedown effects corresponding to

$$(3 \text{ or } 4)d^*4f^15d^26s^2 \rightarrow (3 \text{ or } 4)d^*4f^25d^16s^2 \qquad (3)$$

are always observed in the $3d$ and $4d$ photoemission in Ce-based metallic systems which exhibit moderate to large $4f$ instabilities (see, e.g., Refs. 10 and 11, and references cited therein). The observed $f^1 \rightarrow f^2$ shakedown satellites scale roughly with the degree of "effective mixed valency." Moreover, and particularly relevant to the present study, the shakedown satellites appear with roughly comparable intensity (i.e., within a factor of 2) in La- and Pr-based isomorphs of Ce-based systems which exhibit the shakedowns [e.g., LaSb,[12] $LaPd_3$ and $PrPd_3$,[10] and La (Ref. 13)]. In La and Pr, the $f^0 \rightarrow f^1$ and $f^2 \rightarrow f^3$ shakedowns, respectively, are the analogs of the $f^1 \rightarrow f^2$ shakedown in Ce. Since the $4f$ electron, because of its small orbital radius, provides better screening than a band electron, the observed shakedown satellite is chemically shifted to a lower binding energy than the primary d emission.[14]

We have addressed the question of ground-state versus final-state effects in L_{III} absorption in Ce-based systems by performing L_{III} absorption on the La and Pr isomorphs of a number of Ce-based systems which exhibit double-edge structure. Included in the study were the following mixed-valent systems: $CePd_3$, $CeRu_2$, $CeCo_5$, $CeNi_5$, and $CeNi_2$, and either the La or Pr isomorphs or both. The intermetallics were prepared by arc melting in an inert atmosphere, followed by suitable annealing procedures required to establish a single-crystalline phase as determined by x-ray diffraction. The material was then powdered and hermetically sealed in a suitable tape sandwich, the thickness of the resulting sample falling in a region for which the edge spectra were established experimentally to be thickness independent. The experiments were performed in transmission at the Cornell University synchrotron radiation facility (CHESS), using x rays emitted by the storage ring (CESR) operating at 5.3 GeV. A monochromator using two Si(111) crystals offset by 8 cm and mounted 11 m from the source gave a resolution of about 0.7 eV at the Ce L_{III} edge. The L_{III}-edge spectra are shown in Fig. 1.

The observed spectra for $LaPd_3$, $CePd_3$, $CeNi_2$, and $CeNi_5$ are similar to those reported in Ref. 2. The most important visually apparent result in Fig. 1 is the absence of a second-edge feature in the Pr-based systems. We argue that this result dispels the conjecture[8] that the higher-edge feature observed in Ce-based systems is a result of the shakeup process given by (1). For, if such a shakeup were present in the Ce-based systems it should be present in the Pr isomorphs. In either XPS or x-ray absorption, the intensities of both the shakeup and shakedown features of the types (1) and (2), respectively, relative to the major emission or edge feature, should scale at least to order V/E, where V is the energy of hybridization between the $4f$ electron and the band state and E is the separation in energies of the major feature and the satellite.[15] The ratio of the intensities of the shakeup states in the Ce- and Pr-based systems should be comparable to the ratio of the shakedown satellites in XPS observed for the same systems. The latter conclusion reflects that the quantity $(E_{f1}-E_{f2})/(E_{f0}-E_{f1})$ for Ce-based systems should be roughly proportional to the quantity $(E_{f2}-E_{f3})/(E_{f1}-E_{f2})$ for the Pr isomorphs, where E_{fi} is the energy of the relevant spectral feature.

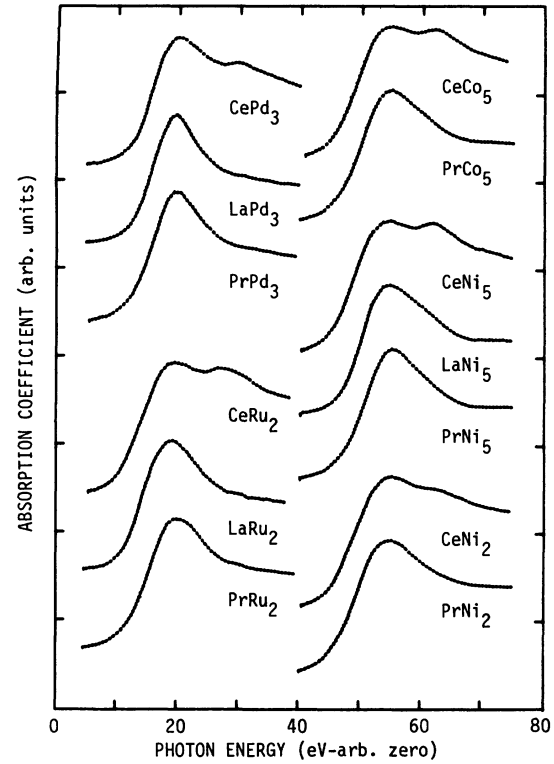

FIG. 1. L_{III}absorption edges for various Ce-, La-, and Pr-based intermetallics. While the scale on the horizontal axis allows the accurate measurement of energy differences in a given spectrum, no effort has been made to accurately determine the absolute energy of the edges (i.e., to determine chemical shifts). The main edges occur within a few volts of the corresponding atomic edges, i.e., Ce(5724 eV), La(5483 eV), and Pr(5965 eV).

We have argued above that the high-energy feature of the double L_{III} edge observed in Ce-based systems is neither due to or altered by shakeup events as suggested by Lengeler *et al.*[8] We now address the question of possible shakedown effects in the spectra of Fig. 1. From $3d$ XPS the ratio of $E_{f2}-E_{f1}$ to $E_{f1}-E_{f0}$ in Ce-based systems has been measured to be roughly $\frac{1}{3}$.[10,11] Hence $f^0 \rightarrow f^1$ shakedown events should be $\leq \frac{1}{3}$ as frequent as $f^1 \rightarrow f^2$ shakedowns. The latter have been reported for numerous Ce-based systems and can be as large as 20% or so of the major f^1 emission.[10,11] Expecting a similar ratio of the final-state separations to hold for the $2p^*$ state and noting that $E_{f1}-E_{f0}$ is roughly 9 eV for the various systems in Fig. 1, we expect $f^1 \rightarrow f^2$ shakedowns, if they exist in the systems studied, to produce an edge at approximately 3 eV on the down-energy side of the primary edges in Fig. 1. The smallness of this energy shift relative to the width of the primary edge precludes a distinct visual signature of a shakedown edge. However, in our attempts to fit the bimodal Ce spectra with two edges, we find it necessary to use a slightly broader edge to fit the f^1 feature than the f^0 feature. A semiquantitative deconvolution of the f^1 feature into two edges allows the possibility of an f^2 shakedown whose intensity may be as large as 10–20% of the f^1 feature. A more quantitative statement, including an exhibition of the f^2 edge shape, which is expected to be different than the f^1 edge shape because of the localized nature of the f^2 final state, requires both higher-precision data and the use as standards of heavy rare-earth isomorphs free of shakedown effects. Such experiments are underway.

In summary, the absence of a double L_{III} edge in Pr-based systems implies that the f^0 feature observed in their Ce isomorphs is unaltered by shakeup effects. On the other hand, we cannot rule out the existence of an f^2 shakedown final state convoluted with the f^1 edge.[16] We have determined that the intensity of such a feature, if present, is not larger than approximately 20% of the f^1 intensity for the systems studied. Correspondingly, any $f^0 \rightarrow f^1$ shakedowns should be $\lesssim (\frac{1}{3})20\%$ of the f^0 intensity. Consequently, the intensity of the f^0 feature observed in Ce-based systems reflects predominantly the ground-state occupany of the f^0 state. The same conclusion with respect to $3d$-XPS spectra in Ce-based systems was reached by Hillebrect and Fuggle.[10]

The nature of the f^0 component of the ground state in Ce-based systems remains an open question. The Anderson lattice[1,15] or promotional model,[1] which equates the f^0 intensity with the fraction of electrons transferred from the $4f$ level to the conduction band, demands a much larger f^0 intensity than observed either in XPS or L_{III} absorption for Ce-based systems which appear to be tetravalent or nearly tetravalent on the basis of lattice-constant and magnetic-susceptibility experiments [e.g., $\mathrm{CeRu_2}$,[1] $\mathrm{CeCo_5}$,[11] $\mathrm{CeNi_5}$,[11] and $\mathrm{CeNi_2}$ (Ref. 11)]. Cursory attempts have been made to reconcile a small f^0 intensity by invoking a Kondo lattice model to describe this class of systems.[17] An alternative approach is being pursued, which explores the possibility of a bimodal distribution in the radial location of f electrons.[18] It appears that at this time the theoretical question is unsettled.

ACKNOWLEDGMENTS

We wish to thank Jon Lawrence and John Fuggle for illuminating discussions. We are also grateful to the staff of CHESS for their willing and able assistance. This work was supported in part by the National Science Foundation under Grants No. DMR-8202726 and No. DMR-7911153.

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