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Photoelectron and bremsstrahlung-isochromat studies of $4f$ levels in γ-Ce, $CeAl_3$, $CeSn_3$, and $CePd_3$

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Bremsstrahlung-isochromat spectra (BIS) show the $4f$ levels in γ-Ce, $CeAl_3$, $CeSn_3$, and $CePd_3$ to be localized. The $4f^2$ states are centered about 5 eV above E_F in all cases. The BIS spectra of γ-Ce, $CeSn_3$, and $CePd_3$ all contain evidence for empty $4f^1$ levels just above E_F. The opinion is expressed, that the position of the occupied $4f^1$ levels still cannot be unambiguously identified.

Cerium and several of its compounds are of special interest because of their anomalous properties when cooled below room temperature or exposed to external pressure.[1] Of the materials studied here, γ-Ce transforms into a volume collapsed and nonmagnetic α phase at low temperatures or under pressure,[2] $CeAl_3$ is known for its peculiar behavior below 2 K,[3] and $CePd_3$ appears to be an intermediate valence compound with a temperature-independent magnetic susceptibility at low temperatures.[4] Finally, in $CeSn_3$ there is an unexplained increase in the d character of the neutron scattering Ce form factor below 40 K,[5] and no magnetic ordering is found at low temperatures[6] whilst recent de Haas—van Alphen experiments revealed the presence of electrons with large effective masses at E_F.[7]

In this paper we report x-ray photoelectron (XPS) and bremsstrahlung-isochromat (BIS)[8] spectra to provide direct information on the $4f$ levels which are usually held responsible for the anomalous properties of these compounds. It is still not established to what extent the Ce $4f$ levels are localized or form bands of extended states.[9] XPS and BIS relate within the same approximation to occupied and empty electronic states, respectively.[10] With the high photon energy (1486 eV) used in this study, the spectra of the extended states in the vicinity of the Fermi energy E_F, can be directly interpreted in terms of densities of states (DOS). In the lanthanides, the exceptional behavior of the $4f$ states usually appears clearly in both kinds of these spectroscopies: *the energy of the 4f levels is a discrete function of the 4f shell population* and a straightforward identification of the $f^n \rightarrow f^{n-1}$ (XPS) and $f^n \rightarrow f^{n+1}$ (BIS) excitations in the experimental spectra is usually possible.[10] The situation is less clear for the occupied $4f$ levels of Ce because of their low cross section with respect to other valence states. The situation is better for BIS, where the intensity is proportional to the density of empty states. We report and discuss our spectra in order to allow others to recognize that problems exist and increase the available experimental data base.

The measurements on the intermetallic compounds were made on bulk polycrystalline samples at 300 K. Clean surfaces were produced *in situ* by repeated scraping with an Al_2O_3 file and checked by XPS. The pure element sample was prepared *in situ* by evaporation deposition. The XPS and BIS spectra of γ-Ce, $CeAl_3$, $CeSn_3$, and $CePd_3$ around E_F are shown in Fig. 1. The XPS spectra are arbitrarily scaled to give the same maximum intensity and the BIS intensities are normalized such that the main structure covers the same area.

All BIS spectra show similar main peak structures above E_F with maximum intensities between 4 and 5 eV. In γ-Ce the discrete $4f^2$ final states can be almost perfectly fitted to experiment with the lowest state $^3H_4$ lying 0.38 eV below the maximum.[10] The observation of $4f^2$ final states so far above E_F indicates that the spectra are dominated by the local character of the $4f^1$ initial states. The

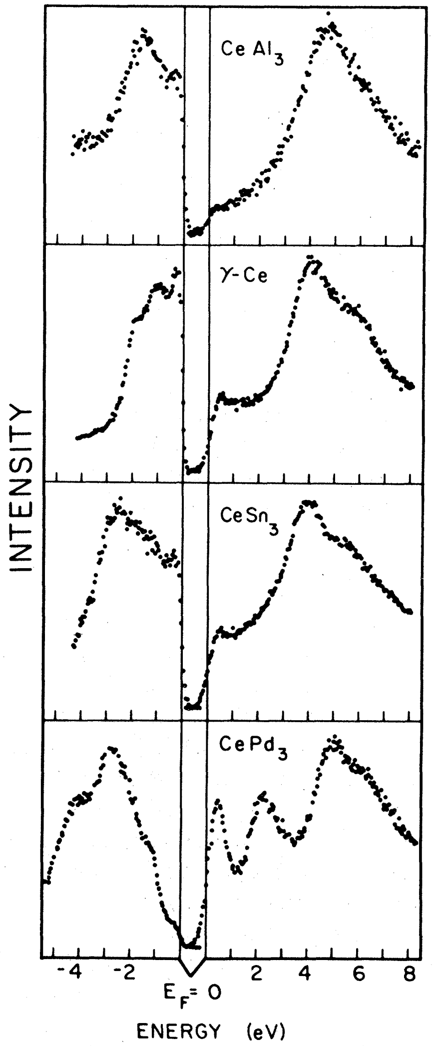

FIG. 1. XPS and BIS spectra around E_F of $CeAl_3$, γ-Ce, $CeSn_3$, and $CePd_3$. The scaling is described in the text.

BIS intensity at E_F is rather low in $CeAl_3$ and must exclusively be attributed to valence states.[11] A much higher intensity with a distinct maximum just above E_F is observed in both γ-Ce and $CeSn_3$. Even after normalizing the areas of the 5-eV peaks, the edge at E_F is roughly two times larger than in La.[10] The simplest interpretation of this intensity at E_F is a weak contribution from *empty* $4f^1$ states, requiring the presence of occupied $4f^1$ states immediately below E_F.

In the BIS spectrum of $CePd_3$, the broad peak at $\sim$ 5 eV and shoulder at $\sim$ 6 eV can be unambiguously attributed to empty $4f^2$ states by analogy with γ-Ce, $CeAl_3$, and $CeSn_3$. Considering the intermediate valence character of $CePd_3$ (Ref. 4) we most naturally assign the peak at 0.45 eV above E_F to $4f^1$ final states. A computer fit locates the lower of the two accessible states, $^2F_{5/2}$, 0.2 eV above E_F. This value is compatible with possible polaronic effects.[12] It is not reasonable to attribute the peak at E_F in $CePd_3$ to empty Pd states as in pure[13] Pd because the density of Pd *d* states at E_F is very low in $CePd_3$ (see below). While the lowest and the highest peak match the expected density of states of a mixed valence compound, the appearance of the peak at 2.25 eV is unexpected and can only tentatively be explained. Since even without a charge transfer from Ce to Pd, the theoretical cross-section ratio[14] between one 4*d* hole and 13 4*f* holes leads to less than $\frac{1}{2}$ of the intensity ratio between this middle peak and the other two, it is unlikely that this additional signal is from empty Pd *d* states. Another possibility is that we are dealing with a surface effect in the sense that the surface Ce ions are trivalent and that their localized levels are shifted as a result of the perturbation by the surface. Such shifts are of the order of 1 eV in CeN.[15] In our case the contribution of the perturbed surface atoms would have to be 25% of the total intensity and the shift about 2.4 eV. The reported temperature dependence of the XPS spectrum of $CePd_3$ could indicate strong surface effects.[16]

Unambiguous assignment of the occupied Ce 4*f* levels in the XPS valence-band spectra is not possible because the cross section for emission of one 4*f* electron is only $\sim$ 0.5 of that for three Ce (5*d* and 6*s*) electrons.[11,14] The 4*f* contribution is smaller in $CeAl_3$ and $CeSn_3$, and its contribution drops below 2% in $CePd_3$.[14] Essentially two alternative positions for the Ce $4f^1$ levels in γ-Ce have been suggested on the basis of photoemission and theoretical studies: approximately 2 eV (Refs. 17—19) and 0 to 1 eV (Ref. 20) below E_F. As the BIS spectra of γ-Ce, $CeSn_3$, and $CePd_3$ all show intensity at E_F which is attributed to empty $4f^1$ states it is natural to look for intensity due to occupied $4f^1$ states just below E_F. In all three materials and even $CeAl_3$, a peak is found just below E_F whose intensity is compatible with emission from 4*f* states. Although this peak is overshadowed in $CePd_3$ by Pd 4*d* states, the integrated signal between E_F and -0.5 eV is more than expected from one localized *f* electron per Ce atom. We also note that this particular intensity is absent in $LaPd_3$.[21] Moreover we deduce from the symmetry of the Pd core level XPS peaks that there is a low density of Pd states at E_F.

If we interpret the spectra of $CePd_3$ such that they simply reveal the mixed valence character through the presence of f^1 (BIS) and f^0 (XPS) final states in a narrow energy range around E_F, we may readily deduce the effective Coulomb correlation energy $U_C = 4.6$ eV. Assuming the f^1 states within 0.4 eV below E_F, similar values are found for the other three materials, namely, 4.5 eV for $CeAl_3$, 3.8 eV for γ-Ce and $CeSn_3$. If the center of these $4f^1$ states has to be positioned at higher binding energies as previously suggested,[17,18] the Coulomb correlation energies take values between 5.5 eV (γ-Ce) and 6.1 eV ($CeSn_3$), which would indicate a rather high variation of U_C with respect to the clear case of $CePd_3$.

Several other facts speak for a $4f^1$ level near E_F in γ-Ce. Our XPS spectrum cannot be reconciled with a $4f$ peak at -2.2 eV with FWHM = 1.6 eV as suggested on the basis of resonant photoemission experiments.[18] The lowest feature in our γ-Ce spectrum is a shoulder at -1.9 eV and the intensity falls off sharply below this energy. We recall that the γ-Ce BIS and the theoretical spectrum with $4f^2$ FWHM = 1.2 eV agreed excellently. In all the rare earths studied so far, the widths of the $4f$ levels vary systematically and the occupied levels are always narrower than the empty levels.[10] Thus a $4f^1$ width > 1.2 eV in γ-Ce would be highly anomalous. If the $4f^1$ level width is indeed less than that of the $4f^2$ level in BIS, then a position about 2 eV below E_F of the former is not compatible with our observation of empty $4f^1$ levels above E_F (see Fig. 1). The position near E_F is also favored by recent band-structure calculations[22,23] and the absence of a peak near E_F in the XPS spectra of La and Pr.[10]

The fact that the $4f$ electrons have localized character in all four substances is demonstrated by the large and discrete energy required for adding an f electron in the BIS process. The same information may, however, also be contained in the Ce $4d$ core level XPS spectra[24,25] (see Fig. 2). The typical multiplet structure shown in Fig. 2 for $CeSn_3$ was also found for $CeAl_3$ (Ref. 11) and γ-Ce (Ref. 26) and reveals the coupling of a $4d$ hole to a localized $4f^1$ electron in the final state. In $CePd_3$ this characteristic multiplet structure is far less well resolved,[24] as in another mixed valent compound, CeN.[26] The apparent broadening of the $CePd_3$ $4d$ spectrum might again be caused by large chemical shifts as discussed above for the interpretation of the BIS spectrum. The unresolved $4d$ spectrum then results from the superposition of two spectra. In order to check this possibility as being realistic, we added two identical spectra of $CeSn_3$, shifted by 2 eV. The result shown in Fig. 2(A) reproduces the salient features of the $CePd_3$ spectrum quite well. However, a large contribution from the screened $4f^2$ final states is identified in the $3d$ XPS spectrum of $CePd_3$ (Ref. 24) and CeN (Ref. 26) so that overlap with the $4d^9 4f^2$ peaks may also be smearing the $4d^9 4f^1$ multiplets.

A contribution of Ce f^0 states in $CePd_3$ (Fig. 2) and CeN is also revealed by the $4d_{3/2,5/2}$ doublet about 10 eV below the main peak[24,26] although its intensity is lower than expected.[24] In $CeAl_3$ (Ref. 11) and $CeSn_3$ the broad structures between -120 and -130 eV are identified as plasmon excitations because similar satellites are associated with the Al and Sn core-level peaks.

In summary these XPS and BIS spectra can be interpreted in terms of narrow ($\sim$1-eV FWHM) localized f states with empty Ce $4f^1$ states just above E_F and $U \sim 4-5$ eV in γ-Ce, $CeSn_3$, and $CePd_3$. The spectra of $CePd_3$ show additional complications which may be due to surface effects.

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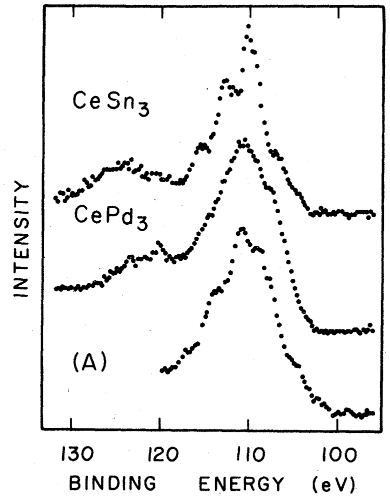

FIG. 2. Ce $4d$ core-level spectra of $CeSn_3$ and $CePd_3$. Spectrum (A) is described in the text.

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