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Nature of Ce $4f$ electronic states from $4d$ excitations in metals and insulators

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We have investigated a variety of metallic and nonmetallic Ce materials by soft-x-ray-absorption spectroscopy at the $N_{4,5}$ thresholds employing the total-electron-yield method. All metallic systems, irrespective of their γ-like or α-like properties, exhibit similar multiplet structures in the prethreshold region, corresponding to $4d^9 4f^2$ final states. In contrast, $4d^9 4f^1$ multiplets are observed for CeF_4 and CeO_2, as in LaF_3, in accordance with the absence of localized $4f$ electrons in the ground states of these compounds. We conclude that tetravalent Ce compounds occur among insulators, but do not exist as metals.

The electronic structure of cerium and its compounds is of much current interest, since it allows the study of a variety of physical phenomena related to the interaction of $4f$ electrons with itinerant electronic states. This aspect of $4f$ interactions has gained importance after the original concept of zero occupancy of localized $4f$ states in α-like Ce systems (e.g., CeO_2, $CeRu_2$) was questioned on the basis of the mixed-valent features observed in deep-core-level photoemission (XPS) and L_3-edge x-ray-absorption (XAS) spectra.[1,2] It was suggested that an upper limit near three exists for the valence of Ce in any chemical environment[3,4] (corresponding to a $4f^1$ cerium ground state). This hypothesis, however, is clearly in conflict with the chemists' view that Ce is tetravalent ($4f^0$) in certain insulators such as CeF_4 and CeO_2. In fact, the results of magnetic, optical,[5] and inverse photoemission[6] measurements show the absence of localized $4f$ electrons in CeO_2. On the other hand, the Kondo volume collapse model of Allen and Martin[7,8] as well as the Anderson impurity theory of Gunnarsson and Schönhammer[9] both predict a Ce valence close to three in metals.

This situation warrants a systematic investigation of metallic and insulating Ce systems with as many experimetal techniques as possible. In the present Rapid Communication, we report the results of systematic soft XAS measurements at the $4d$ thresholds of a variety of Ce compounds, obtained by recording the total electron yield. Soft XAS spectra of several Ce compounds near the $N_{4,5}$ thresholds have been reported previously, using both the conventional absorption technique[10-13] and electron-yield methods,[14-16] as well as the closely related technique of electron-energy-loss spectroscopy (EELS).[17] Until now, however, the only insulating Ce compounds studied were γ-like CeF_3 and Ce_2O_3, as well as α-like CeO_2. The latter is rather unstable, particularly at its surface.[18] Therefore, a major motivation of the present study was to obtain spectra from CeF_4, the most strongly ionic, formally tetravalent Ce compound known, and to compare them to those obtained from metallic systems under similar conditions. The striking result is that all the metallic Ce systems (including extremely α-like Ce compounds such as $CeIr_2$) exhibit very similar fine-structure multiplets below the $4d$ thresholds, which correspond to $4d^9 4f^2$ final states without any indication of $4d^9 4f^1$ spectral features. In the case of insulating α-like Ce compounds, however, such as CeF_4 and CeO_2, predominant peaks arising from the $4d^9 4f^1$ final states are observed. These results indicate that metallic Ce systems do not contain tetravalent Ce, in agreement with theoretical expectations.[7-9] However, tetravalent Ce is observed in insulating α-like Ce compounds. The present results clearly reflect profound differences in the electronic structure of insulating and metallic Ce systems. We also discuss term- and/or threshold-dependent final-state effects, which may influence the $N_{4,5}$ soft XAS spectra.

The experiments were performed in part at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) (Berlin) using the SX-700 monochromator, and in part at the Stanford Synchrotron Radiation Laboratory (SSRL) (Stanford), employing the grasshopper monochromator (beamline III-1). The overall energy resolution was in both cases about 0.1 eV (full width at half maximum). The x-ray-absorption spectra were obtained by recording the total electron-yield signal from the sample surfaces,[19] normalized to the monochromator flux. The intermetallic compounds studied were prepared by arc melting of the elemental components in an Ar atmosphere. The ionic compounds (except CeF_4) were from commerical sources. CeF_4 was prepared from high-purity CeF_3 by reaction at 300 °C with gaseous F_2 at a pressure of 200 atmospheres using a Monel reaction bomb. To the usual limit of sensitivity of the Debye-Scherrer analysis, no impurity phases were detected. All metallic samples and the sintered block of CeF_4 were cleaned *in situ* by scraping with a diamond file in a vacuum of 10^{-10} Torr. The other insulating compounds were dispersed in methanol and painted into 600-wire/in. gold screens on Au-foil backings.

Figure 1 shows soft-x-ray-absorption spectra obtained in the region of the $4d$ threshold for some representative α- and γ-like Ce compounds, as well as from LaF_3 for comparison. The spectra separate clearly into two parts: (i) a low-energy region, with sharp lines of relatively low intensity, below about 115 eV for the Ce compounds, corresponding to excitonic transitions of the type $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ below the $4d$ ionization threshold; and (ii) an adjacent higher-energy region with intense broad peaks, corresponding to similar transitions which end above the $4d$ threshold and are thus strongly broadened by autoionization into the underlying continua.[20,21] The $4d^9 4f^{n+1}$ multiplet extends over more than 20 eV due to the strong $4d$-$4f$ exchange interaction caused by the large radial overlap between the $4d$ and $4f$ orbitals. Calculations of the resulting multiplet structure have been performed earlier within an atomic approximation for the $4d$ and $4f$ states, adjusting the Hartree-Fock parameters to about 70% of their atomic values, in or-

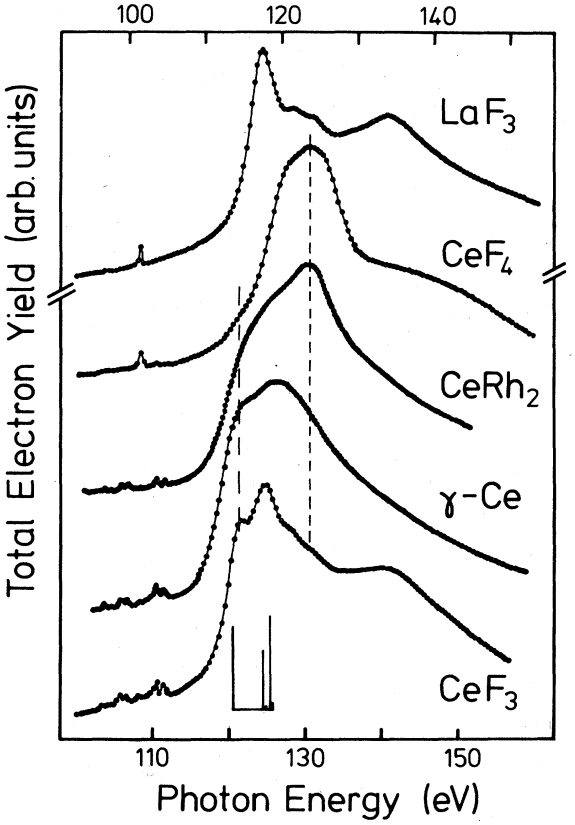

FIG. 1. 4d soft-x-ray-absorption spectra of selected metallic and nonmetallic Ce compounds and (for comparison) of LaF_3, as obtained from total electron-yield measurements. The calculated multiplet components above the 4d ionization threshold (Ref. 22) for the $4d^94f^2$ final-state configuration of Ce are indicated by the bar diagram.

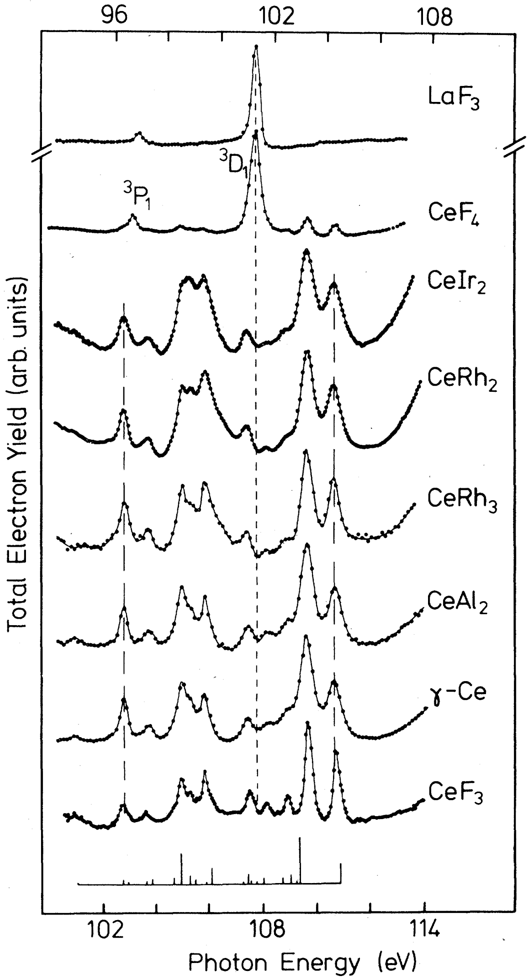

FIG. 2. Fine-structure region of the 4d soft-x-ray-abosorption spectra of several Ce systems and of LaF_3 for comparison. The bar diagram again indicates the calculated multiplet structure of the $4d^94f^2$ final state, here below the 4d ionization threshold. The two optically allowed prethreshold transitions for the $4d^94f^1$ final state are designated in the CeF_4 spectrum.

der to obtain agreement with the measured spectra.[21,22] In this way, a good description of the XAS data was obtained for the $4d^94f^1$ final state in La (three dipole-allowed states at 97, 101, and 117 eV), as well as for the $4d^94f^2$ final state of γ-Ce (26 transitions in the region between 102 and 125 eV.[10-12,23]

As may be seen from Fig. 1, some broadening of the giant resonance structure occurs in going from ionic CeF_3 to metallic Ce materials. Furthermore, the broad feature about 20 eV above threshold is absent in metals. It is characteristic of the rare-earth (R) trihalides and is probably a shape resonance associated with the R—F bond. Comparing the spectra of CeF_4 and CeF_3, we see that the giant resonance maximum of CeF_4 is shifted by about 5 eV to higher energy than that of CeF_3. The CeF_4 spectrum is similar to that observed for CeO_2 (not shown in Fig. 1; see also Refs. 11 and 17). The corresponding features of the giant resonance in $CeRh_2$ appear to be a mixture of γ-like and CeF_4-like structures; they also resemble those of α-Ce metal (Ref. 14). Since the region of the giant resonance is complicated by autoionization processes as well as by the ligand-related states, we first focus our attention on the well-resolved fine-structure patterns below the 4d threshold.

Figure 2 displays the prethreshold fine-structure spectra in more detail for the γ-like systems CeF_3, γ-Ce metal, and $CeAl_2$, as well as for the α-like compounds CeF_4, $CeRh_3$, $CeRh_2$, and $CeIr_2$; the spectrum of LaF_3 is given for comparison. All the spectra shown were corrected for a weakly parabolic background. Figure 2 clearly reveals that there is no essential difference in the observed multiplet structure of all the metallic Ce systems, irrespective of their classification as α-like or γ-like on the basis of magnetic susceptibility, core-level XPS, or L_3-edge XAS data. Similar spectra were obtained for $CeAg_3$, $CePd_3$, and $Ce(Pd_{0.3}Rh_{0.7})_3$ (not shown here). The insulator CeF_3 exhibits the same 4d-4f multiplet structure as the metals, but with a narrower linewidth. The increase in linewidth when going from CeF_3 to $CeIr_2$ is particularly visible in the group of lines near 106 eV; this is a secondary effect which we attribute to increasing 4f hybridization. The present results are in good agreement with those reported in Refs. 14 and 17 (for optically allowed transitions), but do not support the claim made in Ref. 15 that $4d^94f^1$ final-state structures are also observed in the spectra of α-like metallic Ce compounds. This discrepancy may be due to the relatively poor quality of the spectra reported in the latter work.

The situation is totally different in insulating α-like Ce compounds. The prethreshold fine structures observed for CeF_4 and for CeO_2 (not shown) are dominated by two lines at 103 eV ($^3P_1$) and 108 eV ($^3D_1$) expected from a $4d^94f^1$ final state; this is also borne out by the comparison with the spectrum obtained from LaF_3. We rule out an intrinsic origin for the weak $4d^94f^2$ multiplet pattern which is also observed in the spectrum of CeF_4; instead, we attribtute it to sample degradation at the surface. This interpretation is based on the considerable surface sensitivity of the total electron-yield method at photon energies near 100 eV and on the known instability of this compound. In addition, the CeF_4 sample studied was a sintered, slightly porous block, so that not all exposed surfaces could be cleaned by filing. We also note that the CeF_4 spectrum shown was obtained immediately after the completion of vigorous filing of the sample surface; thereafter we observed a strong increase in the $4d^94f^2$ multiplet structure with time. Our CeO_2 spectra showed similar features, which are also certainly not intrinsic. Furthermore, the EELS spectra from CeO_2, recorded under carefully controlled surface conditions (i.e., using residual oxygen pressure during the measurements),[17] did not contain $4d^94f^2$ multiplet structures; the same was true in a recent 4*d* XAS investigation of the dioxide.[13] Thus, there are strong indications for a pure $4d^94f^1$ final-state multiplet structure in CeF_4 and in CeO_2, while all the metallic α-like Ce samples investigated show perfect $4d^94f^2$ final-state patterns with no detectable $4d^94f^1$ features. This result corresponds formally to the absence of localized 4*f* electrons in the ground state of CeF_4 and CeO_2, and $4f^1$ Ce ground states in both insulating and metallic γ-like, as well as metallic α-like Ce systems. This view is further supported by the valence-band photoemission spectrum (4*f*, 5*p*, 5*s*) of CeF_4,[24] which reflects an essentially pure $4f^0$ configuration in the ground state of this compound. The extended states with 4*f* character, which were theoretically predicted for CeO_2 (Ref. 25) (with an effective weight of about 0.5 electrons) are not observed as $4d^94f^2$ final states in the prethreshold XAS spectrum of this compound, nor in that of CeF_4. This is presumably due to their reduced overlap with the 4*d* orbitals.

The increase in linewidth of the prethreshold spectra when going from CeF_3 to γ-Ce metal reflects an increase in 4*f* hybridization. This is not unexpected in view of the negligible overlap between 4*f* and valence-band states in CeF_3,[26] on the one hand, and the immersion of the 4*f* state into the conduction band in γ-Ce metal on the other. Even greater line broadening has been reported for α-Ce metal,[14] and a similar increase in broadening is observed in our spectra of α-like metallic Ce compounds, especially in the structure near 106 eV, as noted above. Therefore, our results are consistent with the idea that hybridization strength, and not 4*f* occupancy, is the quantity which changes significantly between metallic α-like and γ-like Ce systems.

It is strongly suggested by other spectroscopic results for metallic Ce systems, interpreted with the Gunnarsson-Schönhammer theory,[6,9] that the 4*f* occupancy of the initial state of Ce in α-like metallic samples is close to $n_f = 0.8$. Our own XAS results at the $M_{4,5}$ thresholds, obtained mostly on the same samples used in the present work, also support this view.[27] By contrast, the interpretation of the results of various spectroscopies for CeO_2 still seems controversial.

The locking of the Ce valence at a value close to three in metals may be explained by thermodynamic arguments.[3,7,8] In terms of the Kondo volume collapse model,[7] the Ce valence is determined by the minimization of the Gibbs free energy. It follows that the product of the 4*f* occupancy n_f with the Kondo coupling constant J should be a maximum, requiring n_f to be near one. In insulators, this mechanism should not be operable, since the density of states near the Fermi level is zero and no Kondo condensation effects can occur. This would readily explain the existence of insulating Ce compounds with $4f^0$ ground states, in agreement with observation.

The complete lack of any $4d^94f^1$ multiplet structure in the 4*d* prethreshold spectra of metallic Ce systems may be attributable to final-state effects, which make the $4d^94f^1$ configuration unstable in a metallic environment. The lack of conduction electrons in insulating compounds, which could occupy 4*f* screening orbitals, seems to prevent such a supression of $4d^94f^1$ final-state structures in the spectra of the latter.

Final-state effects are obviously less important—or perhaps completely inoperative—in the region of the giant resonance above the 4*d* threshold, since there metallic α-like systems do show spectral features also observed in insulating tetravalent Ce compounds (in particular CeF_4). These giant resonance spectra can be interpreted solely in terms of initial-state effects: The most striking feature is the peak near 130 eV, which was also noted by other authors in both CeO_2 and in α-like metallic systems.[11,14,17] It is shifted by about 5 eV to higher energies relative to the main feature observed for γ-like Ce compounds. This energy shift could be caused by Coulomb interaction between the 4*d* hole and the localized 4*f* electron, but a definite assignment is not possible at present. The main absorption in α-like Ce materials could also result from transitions to extended 4*f*-like states, which are hybridized with valence or ligand orbitals, as suggested in Ref. 16 on the basis of resonant photoemission of oxygen 2*p* electrons in cerium oxides.

The different behavior of the prethreshold and giant-resonance spectral regions for α-like metallic Ce systems, however, may also be due to differences in final-state effects. We suggest two possible mechanisms which might give rise to these apparent differences in final-state screening operative in the two spectral regions: term-dependent and threshold-dependent final-state effects. The former could be caused by the differing radial extensions of the various $4d^94f^1$ final-state terms, causing variations in Coulomb energy and in overlap with nonlocalized electronic states. Theoretical calculations for Xe-like Ce atoms show that the $^1P_1$ term (which is a main contributor to the giant resonance transition) is appreciably more extended than the $^3P_1$ and $^3D_1$ terms of the $4d^94f^1$ configuration.[28] The second possibility is that occupation of a screening orbital above the 4*d* ionization threshold is energetically unfavorable, leading to reduced final-state effects in the giant resonance region. Clearly, more work is necessary to decide between these possibilities. Particularly, detailed resonant photoemission studies in the 4*d* threshold region might be useful.

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