PHYSICAL REVIEW B VOLUME 37, NUMBER 3 15 JANUARY 1988-II

$4f$-ligand hybridization in CeF_4 and TbF_4 probed by core-level spectroscopies

G. Kalkowski,* G. Kaindl, and G. Wortmann
Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany

D. Lentz
Institut für Anorganische Chemie, Freie Universität Berlin, D-1000 Berlin 33, Germany

S. Krause
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Germany

(Received 5 June 1987; revised manuscript received 5 October 1987)

X-ray absorption spectroscopy (XAS) at the $3d$ and $2p$ thresholds as well as $3d$ core-level photoemission (XPS) were used to investigate the electronic structure of CeF_4 and TbF_4. From nonatomic $4f$-related spectral features in the $3d$ XAS spectra, $4f$-ligand hybridization is clearly visible in the case of CeF_4 and—less pronounced—in TbF_4. For the latter compound, L_3-edge XAS data support the view of a finite $4f$ admixture to the Tb—F bonding orbitals, while the L_1-edge spectrum reflects more explicitly tetravalency. From $3d$ XPS measurements, an estimate of $\simeq 12$ eV is obtained for the core-hole–$4f$ Coulomb interaction in TbF_4. The high-energy spectra characterize both fluorine compounds as tetravalent insulators with covalent bonding and clearly show a decrease in $4f$-ligand mixing, i.e., an increase in $4f$ localization, with respect to the corresponding dioxides.

I. INTRODUCTION

The electronic structure of formally tetravalent CeO_2 has been controversially discussed in the past in terms of mixed valency,[1,2] tetravalency,[3] as well as the existence of extended $4f$ states.[4] There seems to be consensus now on covalent admixtures of $4f$ states to the Ce—O bonding orbitals in this compound, amounting to approximately 0.5 electrons per formula unit.[5] This f symmetry in the covalent bonds, however, does not contradict the concept of tetravalency for this compound, since it is consistent with the lack of occupied atomiclike (i.e., localized) $4f$ states in the ground state of CeO_2.[4] On the basis of band-structure calculations it was shown in Ref. 5 that the ionicity of CeO_2 is much lower than four due to the covalent nature of this compound.

The sensitivity of core-level spectra to the nature of the $4f$ states is by now well established,[4,6] and the necessity of a many-body treatment of the final core-hole states has been fully realized.[2,4,7,8] Up to now, theoretical calculations have concentrated mainly on core-level spectra of metallic compounds using a configuration-interaction approach based on the Anderson impurity Hamiltonian.[7] The theoretical understanding of the observed core-level spectra is less advanced for formally tetravalent insulating rare-earth (RE) compounds, like CeO_2, where interpretations of core-level spectra are based either on a cluster model[2] or on a filled-band Anderson model.[8] The most extensive treatment so far of core-level photoemission (XPS) and x-ray absorption (XAS) spectroscopy data for CeO_2 has been presented by Kotani *et al.* using the latter approach.[9,10]

The situation is again less clear for other formally tetravalent RE compounds, in particular for CeF_4,[6,11] PrO_2 and TbO_2.[12-16] The necessity to distinguish this class of materials from metallic mixed-valent systems has recently been pointed out on the basis of core-level spectra for CeF_4.[11] Therefore, a more-detailed understanding of $4f$-ligand mixing in these compounds is highly desirable. This situation provided the impetus for the present work on CeF_4 and TbF_4. XAS spectra were measured at the L and $M_{4,5}$ thresholds of CeF_4 and TbF_4, and $3d$ core-level photoemission spectra were taken for TbF_4. The results confirm the existence of a finite $4f$ admixture to the RE–ligand bonds in both compounds, however, with less weight in the Tb compound. In addition, a comparison with analogous results for the corresponding dioxides[4,12-16] reveals reduced $4f$ admixtures in the tetrafluorides as compared to the dioxides.

II. EXPERIMENT

In the present work, the same CeF_4 sample was used as in our previous L_3 and $N_{4,5}$ XAS and $3d$ XPS studies.[6,11] The TbF_4 sample was prepared by reaction of powdered TbF_3 with fluorine gas in a Monel container at a temperature of 500 K and a pressure of 200 bars.[17] Debye-Scherrer analysis showed that the reaction product had the desired ZrF_4 structure, with only a small amount of TbF_3 impurities present, barely above the limit of detectability. For the $M_{4,5}$ XAS and $3d$ XPS measurements, pellets were pressed from the resulting powder and fixed to Ta substrates. For the L XAS measurements, TbF_4 powder was diluted with B_4C powder and sealed hermetically in a Lucite capsule under purified argon gas; this sample was stored at liquid-nitrogen temperatures.

The XAS spectra at the $M_{4,5}$ thresholds were measured at the double-crystal monochromator (KMC) beam line of BESSY (Berliner Elektromenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.), using a pair of beryl(10$\bar{1}$0) crystals. Resolution at the Ce $M_{4,5}$ thresholds was estimated as $\simeq 0.5$ eV [full width at half maximum (FWHM)].[18] The spectra were taken by recording the total electron yield from the sample surface and relating it to the incoming photon flux, which in turn was measured by the total electron yield from a gold grid between the monochromator exit and the sample. Before each measurement, performed in a vacuum of typically 5×10^{-10} Torr, the sample surface was scraped *in situ* with a diamond file. The L XAS spectra were obtained in transmission geometry at the EXAFS-II beam line of HASYLAB-DESY (Hamburger Synchrotronstrahlungslabor–Deutsches Elektronen-Synchrotron), which was equipped with a double-crystal Si(111) monochromator; in this case, the achieved resolution was $\simeq 1.8$ eV (FWHM). The $3d$ core-level XPS data for TbF$_4$ were taken with a commercial ESCA spectrometer in a vacuum of $\simeq 1\times 10^{-9}$ Torr using nonmonochromatized Al $K\alpha$ radiation. The total system resolution in the XPS measurements was $\simeq 1.6$ eV (FWHM). Again, the sample surface was cleaned repeatedly during the measurements by scraping with a diamond file.

III. RESULTS AND DISCUSSION

A. $M_{4,5}$ XAS spectra of CeF$_4$ and CeO$_2$

XAS spectroscopy at the $M_{4,5}$ thresholds of RE elements is well suited for studies of the $4f$-related electronic structure in RE compounds.[19–22] In heavy-RE systems, the $3d \rightarrow 4f$ core excitation spectra provide direct insight in the electronic ground state of the system.[22] We have therefore applied this type of spectroscopy to the study of CeF$_4$ and TbF$_4$. Figure 1 shows the $M_5(3d_{5/2})$ XAS spectra of CeF$_4$ and CeO$_2$ and—for comparison—that of the trivalent $(4f^1)$ compound CeF$_3$. As shown in detail previously,[23] the shape of the latter spectrum is well described by optical transitions from a $3d^{10}4f^1$ initial state to a $3d^94f^2$ final state in atomic approximation. In all M_5 XAS spectra of formally tetravalent Ce systems measured so far, traces of this final-state multiplet were observed. Since the intensity of this $3d^94f^2$ multiplet, however, was found to be lowest for a freshly scraped surface and increasing gradually with time thereafter, a nonintrinsic origin is most probable.

As shown in Fig. 1, the spectral contributions of these Ce^{3+} impurities were separated from the CeF$_4$ and CeO$_2$ raw data by subtracting an appropriately weighted CeF$_3$ spectrum (dashed lines). The resulting difference spectra (dashed-dotted lines) are assigned to Ce^{4+}, and they are supposed to represent the intrinsic signals from stoichiometric CeF$_4$ and CeO$_2$ materials, respectively. Note the different shapes of the dashed-dotted subspectra in the two formally tetravalent Ce compounds, which deviate both considerably from an atomiclike $3d^94f^1$ final-state multiplet, as observed, e.g., for trivalent La compounds. Such a $3d^94f^1$-M_5 multiplet consists of an intense main line ($^3D_1$) and a rather weak peak ($^3P_1$) at $\simeq 4.3$-eV lower excitation energy.[24] Due to the isoelectronic $3d^{10}4f^0$ ground-state configurations of La^{3+} and Ce^{4+} in the atomic limit, the present M_5 XAS spectra then clearly indicate considerable deviations from atomiclike $4f$ character in these formally tetravalent Ce compounds. However, a certain resemblance of the spectral shapes with that of the La^{3+}-M_5 multiplet cannot be overlooked. If we assign the main resonance line in the Ce^{4+} spectra to the $^3D_1$ state of La^{3+}, a weak peak at $\simeq 4.7$-eV lower excitation energy may be identified as the related $^3P_1$ excitation in both M_5 spectra. The 0.4-eV larger separation between the two final states in the Ce^{4+}-M_5 spectra is caused by the stronger effective core potential in Ce^{4+} as compared to La^{3+}.

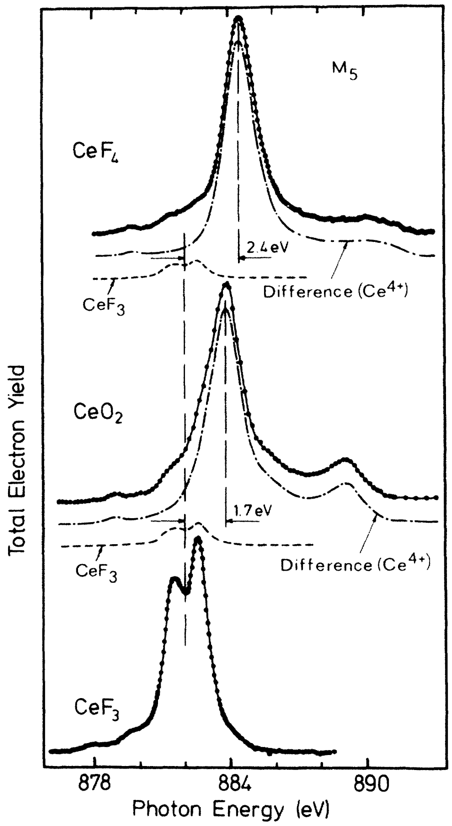

FIG. 1. XAS spectra at the Ce-M_5 threshold of CeF$_4$, CeO$_2$, and CeF$_3$. The spectra of CeF$_4$ and CeO$_2$ are decomposed into the intrinsic Ce^{4+} subspectrum (dashed-dotted line; see text) and a Ce^{3+} impurity component (dashed line). The solid lines through the data points serve as a guide to the eyes.

As mentioned above, essential deviations from the atomiclike La^{3+}-M_5 multiplet are observed, however, on the high-energy side of the main Ce^{4+} line, with different shapes and intensities for CeO$_2$ and CeF$_4$. These satellite features are smeared out up to $\simeq 8$ eV above the main resonance line in CeF$_4$, while they show a distinct maximum at an energy of $\simeq 5.2$ eV above the main line in the CeO$_2$ case. These satellite intensities cannot be obtained from $3d^94f^1$ or $3d^94f^2$ atomiclike multiplets even when dipole-forbidden transitions would become partially allowed due to $4f$ hybridization. This is obvious from the results of full $3d^9 4f^{n+1}$ multiplet calculations[25] as well as from electron-energy-loss spectra.[26] Therefore, these satellite features are thought to represent a fingerprint of the strong $4f$-ligand hybridization in these Ce^{4+} compounds. Related satellite structures were previously reported for $M_{4,5}$ spectra of metallic mixed-valent (α-like) Ce compounds,[19–21] and were theoretically described as many-body final states in an Anderson-impurity model with finite $4f$-electron–conduction-electron hybridization.[7,21]

The spectra in Fig. 1 clearly show a decrease in satellite intensity from CeO_2 ($\simeq 22\%$ of the main line) to CeF_4 ($\simeq 12\%$). Furthermore, the main line is slightly narrower in the CeF_4 spectrum and is also shifted to higher photon energies (by $\simeq 0.7$ eV relative to the CeO_2 spectrum, which in turn is shifted by $\simeq 1.7$ eV with respect to the $3d^9 4f^2$ multiplet of Ce^{3+}). The shift between the M_5 XAS spectra of CeF_4 and CeF_3 (2.4 eV) is of the same magnitude as the separations ($\simeq 2.5$ eV) found previously between $4f^n$ and $4f^{n+1}$ multiplets in homogeneously mixed-valent or stable trivalent and divalent Sm, Eu, and Tm compounds.[20,22] This indicates, to a certain extent, a more atomiclike nature ($3d^9 4f^1$) of the main M_5 resonance line in the CeF_4 spectrum as compared to CeO_2. On the other hand, it should be added here that no shifts of the $3d^9 4f^2$ multiplets beyond experimental accuracy were observed for a large group of stable trivalent (metallic or insulating) Ce compounds,[20] in agreement with the adopted $4f$ occupancies close to 1 in the ground states of these systems.

The crucial question, to what extent the satellite intensity in the XAS final state of CeF_4 is representative of the electronic ground state, cannot be answered in a quantitative way without treating the excitation process within a many-body framework. In a qualitative way, however, the smaller relative weight of the satellite feature in the CeF_4 spectrum, as compared to CeO_2, reflects a lower degree of $4f$-ligand mixing in the former compound. This behavior may actually be expected due to the higher ionicity of this compound.

A quantitative description of the $M_{4,5}$ XAS spectrum of CeO_2 within the filled-band Anderson model has been given recently by Jo and Kotani.[10] Starting from strong f admixtures to the ligand-p band in the ground state of this covalent insulator, these authors come to the conclusion that both the main resonance lines and the satellites contain about equal amounts of $3d^9 4f^1$ and $3d^9 4f^2$ character in the final state, with the weak intensity of the satellite arising mainly from an interference effect. If we adopt an analogous description for CeF_4, the present $M_{4,5}$ spectra characterize this compound as a covalent insulator with less $4f$ admixture to the filled ligand band than in CeO_2.

A decrease in covalent $4f$-ligand mixing from CeO_2 to CeF_4 is also consistent with previously reported soft-XAS spectra at the $N_{4,5}$ thresholds ($4d \to 4f$ excitations) of the two compounds.[6,27] These spectra are characterized by a broad "giant" resonance and narrow prethreshold multiplet lines, dominated in this case ($4d^9 4f^1$ multiplet) by a $^3D_1$ resonance peak. Recent high-resolution measurements for CeO_2 (Ref. 27) have confirmed a larger width of the $^3D_1$-related peak as compared to the spectrum of CeF_4,[6] supporting our conclusion from the present M_5 results for CeO_2 and CeF_4 with respect to a hybridization-induced line broadening.

B. $M_{4,5}$ XAS spectra of TbF_4

Possible $4f$ admixtures to ligand bonds in TbF_4, a formally tetravalent "heavy-RE" compound, may be studied in an analogous way by XAS spectroscopy at the $M_{4,5}$ thresholds. The relevant spectra of TbF_4 and—for reasons of comparison—also of TbF_3 and GdF_3 are displayed in Fig. 2. Since Tb^{4+} and Gd^{3+} have the same $4f^7$ ground-state configurations in atomic approximation, closely related shapes of the final-state $3d^9 4f^8$ multiplets are expected, in analogy to the case of Ce^{4+} and La^{3+} discussed above. As can be seen from Fig. 2, the shape of the spectrum observed for TbF_4 indicates a much larger Tb^{3+} impurity component than observed for CeF_4 (see spectral decomposition in Fig. 1). This is definitely a consequence of the known instability of TbF_4 in high vacuum.[17] The intrinsic Tb^{4+} spectrum (dashed-dotted line) was obtained by subtracting an appropriately weighted TbF_3 signal (dashed line) from the measured TbF_4 spectrum. From an inspectrion of Fig. 2 it is obvious that the dashed-dotted intrinsic TbF_4 spectrum is quite similar in shape to the one of GdF_3. As in the Ce^{4+} case, however, there are also substantial differences; in particular, the pronounced peak at $\simeq 5$ eV above the main M_5 absorption line in GdF_3 (indicated by an arrow) is missing or smeared out in the TbF_4 spectrum. Furthermore, a broad tail is observed at the low-energy side of the M_5 absorption peak in TbF_4, which is not visible in the GdF_3 spectrum. The absence of the 5-eV peak in the TbF_4 spectrum is not related to the different core potential of Tb^{4+} as compared to Gd^{3+}, since it has also been observed in isoelectronic divalent

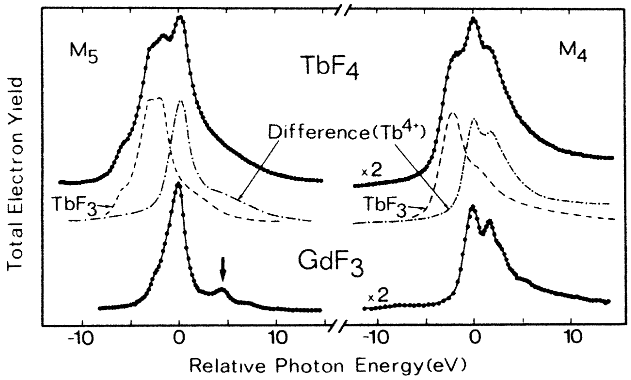

FIG. 2. $M_{4,5}$ XAS spectra of TbF_4, GdF_3, and TbF_3. The intrinsic Tb^{4+} subspectra (dashed-dotted line) are obtained from the measured TbF_4 spectra by subtracting the appropriately weighted TbF_3 spectra (dashed line). The solid lines through the data points serve as a guide to the eyes. Note the different ordinate scales (by a factor of 2) for the M_4 and M_5 spectra.

Eu compounds.[20] We rather suppose that the absence or smearing out of this feature in the TbF_4 spectrum is due to $4f$-ligand mixing, quite similar to the cases of CeF_4 and CeO_2. A close inspection of the right-hand side of Fig. 2 reveals also a small deviation of the intrinsic M_4 XAS spectrum of TbF_4 from that of GdF_3; this deviation is less pronounced than at the M_5 threshold, presumably due to the broader linewidths at M_4 as compared to M_5.[24]

Support for this interpretation of the TbF_4 data is provided by recent XAS measurements at the $M_{4,5}$ thresholds of TbO_2,[14,15] where deviations in the observed $M_{4,5}$ spectral shapes from those of Gd^{3+} compounds were also observed. In TbO_2, additional broad shoulders show up at $\simeq 3$ eV above the absorption maxima of both M_5 and M_4 spectra, similar to the satellite peak of CeO_2 described above. If we regard these features as a consequence of strong $4f$-ligand mixing in analogy to the case of tetravalent Ce compounds, their absence in the TbF_4 spectrum suggests again a more-localized $4f$ character in the tetrafluoride as compared to the dioxide.

C. $L_{1,3}$ XAS spectra of TbF_4

The apparently weak $4f$ admixture to the Tb—F bonds in TbF_4 may be probed more efficiently by XAS at the L thresholds, since the involved optical processes correspond to exciting a core electron into extended states with mostly d ($L_{2,3}$) or p (L_1) symmetry outside of the atomic core. In this way, final-state relaxation processes of valence orbitals should be enhanced as compared to $3d$ XAS. Figure 3 shows XAS spectra of TbF_4 and TbF_3 at the L_3 and L_1 thresholds recorded in standard transmission geometry.

For TbF_3, an intense absorption peak is observed at L_3, which is characterized by a "white line" due to electronic transitions into unoccupied electronic states of mainly $5d$ character, plus a relatively weak "edge jump" corresponding to transitions into continuum states with d or s symmetry. This "atomiclike" trivalent L_3 XAS spectrum was analyzed by a least-squares fit of a Lorentzian (short-dashed line) plus an arctan function to the data, as indicated in Fig. 3, resulting in an intrinsic Lorentzian width of 4.5 eV (FWHM).

The corresponding white line of the TbF_4 L_3 XAS spectrum (see Fig. 3) is much broader and exhibits several shoulders (denoted by B, C, and D) besides the maximum (A). In particular, a shoulder (D) is observed at the position of the white line of TbF_3, signaling the presence of TbF_3 impurities in the spectrum of TbF_4. The relative intensity of this feature (short-dashed line) is much smaller than the related TbF_3 spectral component in the $M_{4,5}$ XAS spectrum. This is readily understandable from the instability of TbF_4 and the fact that the L XAS spectra were measured in transmission geometry on a bulk sample hermetically sealed under argon atmosphere and kept at liquid-nitrogen temperature, while the $M_{4,5}$ data had to be taken in a surface-sensitive way on a sample in vacuum. In the L_3 XAS spectrum of TbF_4, a weak peak C (dotted line) is also noticeable at the onset of the white line, similar to observations made in the L_3 XAS spectra of all tetravalent RE compounds studied so far.[1,11–14,16] The TbF_4 spectrum was analyzed by a superposition of four subspectra (each described by a Lorentzian plus an arctan function), in analogy to the TbF_3 spectrum. In the least-squares fit, the spectral shapes of two of the subspectra (short-dashed and dotted lines) were set equal to that of TbF_3, while those of the other two subspectra were described by free fit parameters for linewidth and relative intensity of the white line.

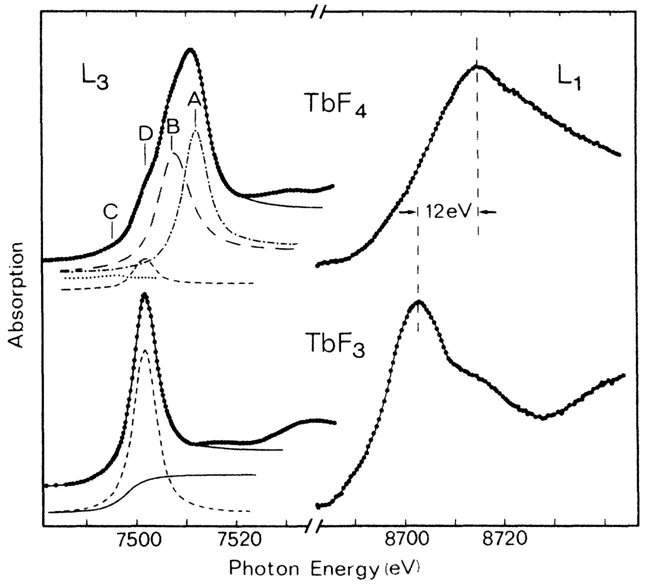

FIG. 3. XAS spectra of TbF_3 and TbF_4 at the L_3 and L_1 thresholds of Tb. The solid lines through the data points of the L_3 spectra represent the results of least-squares fits by a superposition of Lorentzian lines and arctan-like edge structures (see text). In case of the L_1 spectra, the solid lines through the data points serve as a guide to the eyes.

The result of this fit analysis of the L_3 XAS spectrum of TbF_4 is presented in Fig. 3 (solid line through the data points); it bares close similarity with the known L_3 spectra of CeO_2 and CeF_4.[1,11] The total white-line intensity is found to be distributed over the four Lorentzian lines corresponding to peaks A, B, C, and D, with relative intensities of $\simeq 49\%$, 43%, 1%, and 7%, respectively. Furthermore, peak B (A) is found to be shifted by $+5.7$ eV ($+9.9$ eV) relative to peak D, and is about 60% (20%) wider than the latter one. The larger weight of peak A in the present TbF_4 case as compared to CeF_4 (Ref. 11) implies a less-hybridized $4f$ character of the TbF_4 bonds, if we follow the arguments given previously for CeF_4 and CeO_2.[9,11,28] There, the narrow peak A was assigned to an almost pure $2p^5 4f^0 6d^1$ final state, while the broader component B was assumed to reflect the many-body character of final states containing both $4f^1$ and $4f^2$ configurations with ligand orbitals. Note that, in particular, the broad peak B has probably a more complex shape than assumed in the present analysis, since it is associated with ligand-$4f$ charge transfer in a core-hole screening process.[13] We emphasize that the shape of the L_3-edge XAS spectrum of TbF_3 is very similar to that of TbO_2,[14,16] where peaks A and B, however, are better resolved. Even though a least-squares-fit analysis has not been given for the TbO_2 spectrum, we realize that this apparently higher resolution is caused by a larger A-B separation. This then parallels the observations made for CeF_4 and CeO_2 discussed above.[11,28]

The weak feature C in the L_3-edge XAS spectrum of TbF_4 warrants some further comments. Such a weak feature located $\simeq 7$ eV below the trivalent component D has been observed in all L_3-edge XAS spectra of formally tetravalent Ce, Pr, and Tb compounds recorded so far. The width of peak C ($\simeq 2$ eV) was always found to be somewhat narrower than of the other spectral features. These observations practically exclude a $2p \rightarrow 6s$ transition as a possible origin for it. We propose instead a different mechanism for peak C, namely an optically forbidden $2p \rightarrow 4f$ transition, which may contribute as a consequence of d admixtures to the unoccupied f states mediated through the ligand orbitals. The energetic position of peak C is then readily understood from an increased core-hole–$4f$ Coulomb attraction, which is expected to pull this final state with appreciable $2p^5 4f^9$ character well below the L_3 XAS threshold. Our interpretation is supported by related pre-edge resonances observed in XAS spectra at the K thresholds of $3d$–transition-metal compounds, which were interpreted in an analogous way as a consequence of $s \rightarrow d$ transitions into unoccupied d states with strong p admixtures.[29]

On the right-hand side of Fig. 3, the XAS spectra at the L_1 threshold of TbF_4 and TbF_3 are also given. Each of the two spectra is dominated by a relatively broad white-line peak, which is shifted by $\simeq 12$ eV in TbF_4 as compared to TbF_3. An energy difference of similar magnitude was also observed for the edge positions, which were taken as the maxima in the first-derivative curves. These shifts are essentially given by the difference in $2s$-$4f$ Coulomb energy between TbF_4 and TbF_3, since the rather extended final-state $6p$ orbitals are not contributing much to the energy position via repulsive $6p$-$4f$ and attractive $6p$-$2s$ Coulomb energies. The spatial extension of the $6p$ states, particularly in relation to the $5d$ states, should thus cause different core-hole screening effects in the L_1 spectrum as compared to L_3, where the $5d$-$4f$ and $5d$-$2p$ Coulomb energies are considered to be important.[9] In this way, it seems that the tetravalency of TbF_4 shows up in a more direct way in the L_1 spectrum as compared to L_3 and may be more directly related to $3d$ XPS spectra. Analogous observations have been made in the L_1 XAS spectra of CeF_4 and CeF_3.[28]

The close similarity of the TbF_4 and TbO_2 L_3-edge spectra with those of CeF_4 and CeO_2 gives clear evidence of analogous $4f$-ligand mixing in the "heavy-RE" (Tb) and "light-RE" (Ce) formally tetravalent insulating RE compounds. On the other hand, there is no clear evidence for the existence of metallic mixed-valent Tb systems at the moment. Whether this difference between metallic Ce and Tb systems is related to a reduced hybridization strength for the "heavier" RE compound, as suggested from the L_3-edge XAS spectra, or indicative of some basic difference in the $4f$-mixing mechanism of metals and insulators, has to be further investigated.

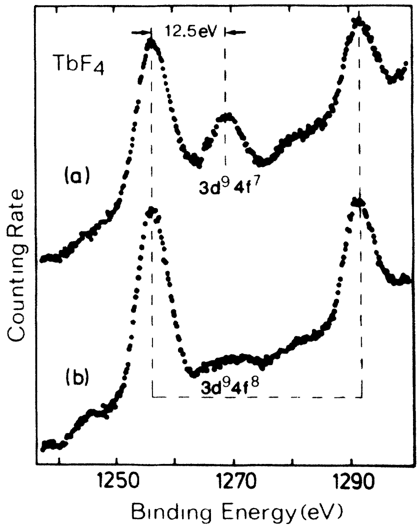

FIG. 4. $3d$ XPS spectrum of TbF_4 accumulated (a) within 15 min and (b) past 80 min after filling of the sample surface in UHV.

D. $3d$ XPS spectrum of TbF_4

Finally, to enlarge the systematics of core-level photoemission data on formally tetravalent RE compounds, we have investigated the $3d$ levels of TbF_4 by XPS. Figure 4(a) shows the accumulated spectral intensity within 15 min after filing of the sample; Fig. 4(b), past 80 min after completion of filing. The latter spectrum is considered largely representative of TbF_3 due to the known decomposition of the sample surface in high vacuum.[17] From the difference of the two spectra, the $3d^9 4f^7$-related multiplet of TbF_4 is clearly identified at a binding energy $\simeq 12.5$ eV higher than that of the $3d^9 4f^8$ multiplet of TbF_3. Assuming the absence of appreciable chemical shifts between the two compounds, in analogy to oxygen-deficient CeO_2,[30] and neglecting possible influences from the many-body character of the final states, the spectra provide an estimate of $\simeq 12$ eV for the $3d$-core-hole–$4f$ Coulomb interaction energy. This value is of similar magnitude as in formally tetravalent Ce systems[4,7–9] and is consistent with the outlined parallel features in the electronic structure of formally tetravalent insulating Ce and Tb compounds. Note also the approximate equality of the $3d$-$4f$ and $2s$-$4f$ Coulomb energies of the core holes created in $3d$ XPS and L_1 XAS excitations, respectively.

IV. CONCLUSIONS

In summary, we have given evidence for the presence of nonatomic $4f$-electron features in the $3d$ XAS spectra of the covalent, formally tetravalent insulators CeF_4 and TbF_4. The observed spectral shapes are interpreted as signatures of relatively strong $4f$-ligand mixing in the ground states of both compounds. This result is corroborated by a study of the L_3-edge XAS spectrum of

TbF$_4$ and a comparison with previously published L_3 XAS data for CeF$_4$ and the dioxides. A smaller spectral weight of the nonatomic features in the spectra of CeF$_4$ and TbF$_4$, as compared to those of CeO$_2$ and TbO$_2$, is related to a higher ionicity, i.e., a more-localized nature of the 4f states in the tetrafluoride compounds. The 3d XPS spectra of TbF$_4$ and TbF$_3$ lead to an estimate of $\simeq 12$ eV for the core-hole–4f Coulomb interaction in formally tetravalent Tb compounds, which is of similar magnitude as found for Ce systems. Our observations indicate a close analogy in the 4f-ligand mixing mechanism operative in formally tetravalent insulating compounds of light and heavy rare earths, respectively.

In a recent publication,[15] the nonatomic satellite peaks observed in $M_{4,5}$ XAS spectra of CeO$_2$, PrO$_2$, and TbO$_2$ have been interpreted as due to transitions into "extended" 4f states. This terminology is related to a controversial claim by Schlüter and Varma,[31] based on Thomas-Fermi calculations, that a double-well potential may also exist in a solid. Even though such a potential for 4f electrons is well known for free atoms to occur, its relevance to solids has been strongly questioned.[32] The clue to this "extended-4f-state" controversy[4,33,15] may be provided by identifying extended 4f states in a solid with the covalent f-symmetry admixture to the ligand band.[5,11] It seems that the "interatomic mixed valency" defined in Ref. 13 may well fit in this category. In deep core-level spectroscopies, the initial state is coupled to the different many-body final states containing a deep core hole. The question then is, whether present configuration-interaction theories are capable of describing these final states sufficiently well or if some features, as, e.g., the increased radial extent of these states, require a separate treatment. An indication for the latter is provided by the energy positions of the main $M_{4,5}$ XAS resonance lines and their satellites in the spectra of α-like metallic Ce compounds and formally tetravalent covalent compounds of Ce.[19] It is striking that the satellite peaks in α-like metallic Ce compounds (e.g., CeRh$_3$) and in CeO$_2$ are both shifted by $\simeq 5$ eV relative to the main $M_{4,5}$ resonances, irrespective of the exact position of these main resonances and the nature of the ligands. The addressed question is definitely of enough importance to warrant further experimental and theoretical work in this direction.

ACKNOWLEDGMENTS

The authors acknowledge support by Dr. E. V. Sampathkumaran and Dr. K. Horn as well as fruitful cooperation with the staffs of the Berliner Elektromenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) and the Hamburger Synchrotronstrahlungslabor (HASYLAB). This work was supported by the Bundesminister für Forschung und Technologie, Project No. 05 313 AXB2, TP4.

---

*Present address: Siemens AG, Rohrdamm 88, D-1000 Berlin 33, Germany.

[1] K. R. Bauchspiess *et al.*, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and B. Maple (North-Holland, Amsterdam, 1981), p. 417.

[2] A. Fujimori, Phys. Rev. B **28**, 2281 (1983).

[3] F. Marabelli and P. Wachter, Phys. Rev. B **36**, 1238 (1987).

[4] E. Wuilloud, B. Delley, W. D. Schneider, and Y. Baer, Phys. Rev. Lett. **53**, 202 (1984); W. D. Schneider, B. Delley, E. Wuilloud, J. M. Imer, and Y. Baer, Phys. Rev. B **32**, 6819 (1985).

[5] D. D. Koelling, A. M. Boering, and J. Wood, Solid State Commun. **47**, 227 (1983).

[6] G. Kalkowski, C. Laubschat, W. D. Brewer, E. V. Sampathkumaran, M. Domke, and G. Kaindl, Phys. Rev. B **32**, 2717 (1985).

[7] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

[8] A. Kotani, H. Mizuta, T. Jo, and J. C. Parlebas, Solid State Commun. **53**, 805 (1985).

[9] T. Jo and A. Kotani, Solid State Commun. **54**, 451 (1985); A. Kotani and T. Jo, J. Phys. (Paris) Colloq. **47**, C8-915 (1986).

[10] T. Jo and A. Kotani, J. Phys. Soc. Jpn. **55**, 2457 (1986).

[11] G. Kaindl, G. K. Wertheim, G. Schmiester, and E. V. Sampathkumaran, Phys. Rev. Lett. **58**, 606 (1987).

[12] R. C. Karnatak, M. Gasgnier, H. Dexpert, J. M. Esteva, P. E. Caro, and L. Albert, J. Less-Common Met. **110**, 377 (1985).

[13] A. Bianconi, A. Marcelli, H. Dexpert, R. Karnatak, A. Kotani, T. Jo, and J. Petiau, Phys. Rev. B **35**, 806 (1987).

[14] J. M. Esteva, R. C. Karnatak, H. Dexpert, M. Gasgnier, P. E. Caro, and L. Albert, J. Phys. (Paris) Colloq. **47**, C8-955 (1986).

[15] R. C. Karnatak, J.-M. Esteva, H. Dexpert, M. Gasgnier, P. E. Caro, and L. Albert, Phys. Rev. B **36**, 1745 (1987).

[16] H. Dexpert, R. C. Karnatak, J.-M. Esteva, J. P. Connerade, M. Gasgnier, P. E. Caro, and L. Albert, Phys. Rev. B **36**, 1750 (1987).

[17] H. O. Haug and G. Hansmann, Karlsruhe Nuclear Research Center Report No. 1325, Karlsruhe, Germany, 1971 (unpublished).

[18] J. Feldhaus, F. Schäfers, and W. Peatman, SPIE Proc. **733**, 242 (1987).

[19] G. Kaindl, G. Kalkowski, W. D. Brewer, B. Perscheid, and F. Holtzberg, J. Appl. Phys. **55**, 1910 (1984).

[20] G. Kaindl, G. Kalkowski, W. D. Brewer, F. Holtzberg, and A. Schach von Wittenau, J. Magn. Magn. Mater. **47&48**, 181 (1985).

[21] J. C. Fuggle, F. U. Hillebrecht, J. M. Esteva, R. C. Karnatak, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 4637 (1983).

[22] G. Kaindl, W. D. Brewer, G. Kalkowski, and F. Holtzberg, Phys. Rev. Lett. **51**, 1910 (1984).

[23] J. Sugar, W. D. Brewer, G. Kalkowski, G. Kaindl, and E. Paparazzo, Phys. Rev. A **32**, 2242 (1985).

[24] C. Bonnelle, R. C. Karnatak, and J. Sugar, Phys. Rev. A **9**, 1920 (1974).

[25] B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J. M. Esteva, Phys. Rev. B **32**, 817 (1985).

[26] J. A. D. Matthew, G. Strasser, and P. Netzer, Phys. Rev. B **27**, 5839 (1983).

[27] T. Hanyu, H. Ishii, M. Yanagihara, T. Kamada, T. Miyahara, H. Kato, K. Naito, S. Suzuki, and T. Ishii, Solid State Commun. **56**, 381 (1985).

[28] G. Schmiester, Ph.D. thesis, Freie Universität Berlin, 1987 (unpublished). This work gives further evidence for a nonintrinsic origin of peak *D* in the L_3-edge XAS spectra of tetravalent Ce compounds.

[29] See, e.g., K. H. Frank, E. E. Koch, and H. W. Biester, J. Phys. (Paris) Colloq. **9**, C8-653 (1986).

[30] J. W. Allen, J. Magn. Magn. Mater. **47&48**, 168 (1985).

[31] M. Schlüter and C. M. Varma, Helv. Phys. Acta **56**, 147 (1983).

[32] A. Bringer, Solid State Commun. **46**, 591 (1983).

[33] A. Fujimori, Phys. Rev. Lett. **53**, 2518 (1984); E. Wuilloud, B. Delley, W.-D. Schneider, and Y. Baer, *ibid.* **53**, 2519 (1984).