PHYSICAL REVIEW B VOLUME 38, NUMBER 14 15 NOVEMBER 1988-I

Pressure-induced changes in $L_{\rm III}$ x-ray-absorption near-edge structure of CeO_2 and CeF_4: Relevance to $4f$-electronic structure

G. Kaindl, G. Schmiester, E. V. Sampathkumaran*
Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany

P. Wachter
Laboratorium für Festkörperphysik, Eidgenössiche Technische Hochschule, CH-8093 Zürich, Switzerland

(Received 23 August 1988)

X-ray-absorption near-edge structure (XANES) studies were performed at the $L_{\rm III}$ thresholds of CeO_2 and CeF_4 as a function of external pressure up to ≃267 kbar at room temperature. In both cases, the $4f^0$-related higher-energy component of the essentially double-peaked XANES structure decreases in relative intensity with pressure, opposite to what is generally observed for metallic mixed-valent Ce compounds. This supports the proposed peak assignment on the basis of core-hole induced many-body effects due to $4f$-ligand covalency compatible with traditional tetravalency of these compounds.

Among the experimental methods employed in determining the valency of rare-earth (RE) ions in solid compounds, x-ray-absorption near-edge structure (XANES) studies at the RE $L_{\rm III}$ thresholds play an essential role due to simplicity and universal applicability.[1,2] The derivation of $4f$ occupancies in the ground state (RE valency) from the measured $L_{\rm III}$ XANES spectra, however, is not free of ambiguities, particularly in mixed-valent or $4f$ covalent compounds. In the most simplistic way, RE valencies have been derived from the usually double-peaked $L_{\rm III}$ XANES spectra of such systems by assuming them to represent a one-to-one image of localized $4f^n$ and $4f^{n-1}$ configurations in the ground state.[2] Such an approach, however, has been shown to be ill-founded both by the experimental observation of core-hole induced final-state changes in $4f$ occupancies even in systems of the heavy rare earths[3-7] and by the theoretical analysis of $L_{\rm III}$ XANES spectra in the framework of the Anderson impurity model.[8,9]

The $L_{\rm III}$ XANES spectra of insulating, formally tetravalent Ce compounds like CeO_2, $Ce(SO_4)_2$, and CeF_4 have been reported to exhibit essentially double-peaked structures (see Fig. 1, peaks A and B), with two additional weak components (peaks C and D in Fig. 1) at lower excitation energies.[2,5-7,10] This spectral shape originally led Bauchspiess *et al.* to claim the nonexistence of tetravalent Ce compounds.[10] Since then, considerable efforts have been made towards a better understanding of the $L_{\rm III}$ XANES profiles of CeO_2 and of other insulating tetravalent Ce compounds. The proposals brought forward may be classified in three categories: (i) Peaks A and B are assumed to directly reflect the Ce^{4+} $4f^0$ and Ce^{3+} $4f^1$ components in the ground state of CeO_2, leading to a mean valency of ~3.32.[10] (ii) Both peaks A and B are assigned to Ce^{4+} $4f^0$ and both peaks D and C to Ce^{3+} $4f^1$, with the A-B and D-C energy separations postulated as originating from ligand-field splitting of the unoccupied Ce $5d$ states. This model leads to mean valencies of

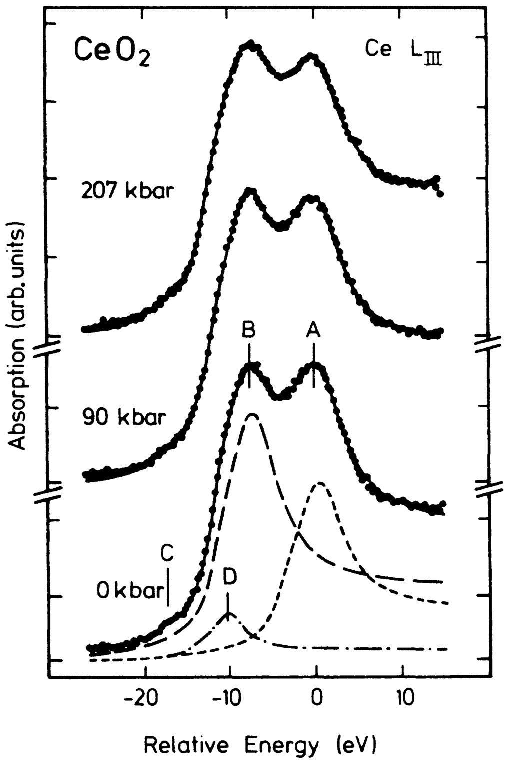

FIG. 1. Room-temperature Ce $L_{\rm III}$ XANES spectra of CeO_2 at ambient pressure, 90 kbar, and 207 kbar. The solid lines are the results of least-squares fits of a superposition of four subspectra to the data. Each subspectrum represents the sum of a Lorentzian and an arctan function convoluted by a Gaussian spectrometer function. The two intense components A and B as well as the weaker component D are given by dashed, long-dashed, and dash-dotted lines, respectively. The position of an additional weak component C is indicated by a vertical bar. Zero of the relative energy scale is set at the position of component A (at ~5.74 keV).

© 1988 The American Physical Society

~3.65 for CeO_2 and ~3.85 for CeF_4 (Refs. 2 and 11). While proposals (i) and (ii) are pure initial-state models, the third category of approaches takes many-body effects in the sense of core-hole-induced changes of $4f$ occupancies in the final state into account.[5,6] (iii) In this model, peak A corresponds essentially to the Ce^{4+} $4f^0$ component in the ground state, while peak B arises from the occupation of localized $4f$ orbitals in the core-excited final state via $4f$-ligand covalency. This model leads to the conclusion that Ce is essentially tetravalent in CeO_2 and CeF_4. Recent theoretical calculations of many-body effects in the Ce $L_{\rm III}$ XANES spectra of CeO_2 (Ref. 8) and CeF_4 (Ref. 9) illustrate the nonexistence of a one-to-one correspondence between the peak intensities in Ce $L_{\rm III}$ spectra and the $4f$ occupancies (valence) in the ground state, thus supporting model (iii).

In view of these fundamental discrepancies in the assignment of peaks in Ce $L_{\rm III}$ XANES spectra of insulating formally tetravalent Ce compounds, an urgent need for additional experimental information suitable for a clarification of the controversy is obvious. In this communication, we present such data in the form of high-pressure Ce $L_{\rm III}$ XANES spectra of CeO_2 and CeF_4 for external pressures up to ~267 kbar. In both cases we find an appreciable decrease in the relative intensities of the $4f^0$-related $L_{\rm III}$ components A with increasing pressure, which is opposite to what has generally been observed and is actually expected for mixed-valent Ce compounds.[2] The results therefore rule out the proposals of categories (i) and (ii) and strongly support the models of category (iii) that include final-state effects via a strong $4f$-covalent mixing in the ground state that is supposed to increase with pressure.[5,6,8,9]

The XANES measurements at the Ce $L_{\rm III}$ threshold ($h\nu \simeq 5740$ eV) were performed in transmission geometry at the EXAFS-II beamline of HASYLAB in Hamburg, West Germany, which is equipped with a Si(111) double-crystal monochromator. External pressures up to ~267 kbar could be applied to the samples by use of a diamond-anvil high-pressure setup. Through the use of slitted Be gaskets, it was possible to let the synchrotron radiation pass the opposed-anvil setup in a direction perpendicular to its axis. The samples employed in the present investigation were taken from the same batches as those used in previous studies of CeF_4 (polycrystalline) and CeO_2 (single crystal).[12] Since CeF_4 is known to deteriorate upon exposure to air, specific care was taken in preparing homogeneous absorber foils from finally powdered material and epoxy resin in purified Ar atmosphere.

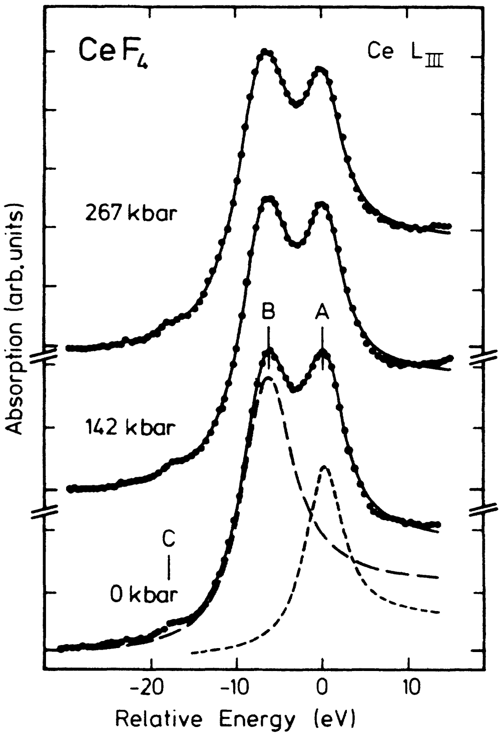

FIG. 2. Room-temperature Ce $L_{\rm III}$ XANES spectra of CeF_4 at ambient pressure, 142 kbar, and 267 kbar. The nomenclature is the same as in Fig. 1. Note that a component corresponding to feature D in the spectrum of CeO_2 is missing.

Typical $L_{\rm III}$ XANES profiles of CeO_2 and CeF_4 as a function of external pressure are displayed in Figs. 1 and 2. As is well known by now,[2,5,10] the spectra are characterized by two intense absorption peaks A and B plus an additional weak feature C at lower excitation energy, in addition to the steplike absorption threshold. While the latter is caused by optical transitions from the $2p$-core state into empty continuum states with s and d symmetry, the individual peaks (called white lines) reflect transitions into more localized empty final states: $5d$ states in the case of peaks A and B (optically allowed) and possibly $4f$ states (optically forbidden) in the case of the weak pre-edge feature C (Refs. 6, 13, and 14). Only in the case of CeO_2 is a fourth weak component D found in the present work. The D component intensity varies from sample to sample and also with the absorber preparation method.[5,15] A peak at position D is also observed for CeF_4 if a different absorber preparation method, using, e.g., paraffin instead of epoxy, is applied.[5,15] Since the position of peak D, in addition, coincides in energy with the single prominent white-line XANES peak of trivalent Ce compounds, e.g., Ce_2O_3 and CeF_3, one has to conclude unequivocally that peak D, if observed, is due to Ce^{3+} impurities in the sample and does not represent an intrinsic feature of the $L_{\rm III}$ XANES spectra of CeF_4 and CeO_2. Naturally, these observations render the peak assignment of Röhler *et al.*[2,11] [model (ii)] groundless since peaks C and D cannot represent the ligand-field split $\underline{2p}4f^15d^*$ final state, as claimed ($\underline{2p}$ = hole in Ce $2p$ core state).

A closer inspection of the results of the least-squares fits of the spectra of Figs. 1 and 2 supports the above conclusion. While the fractional intensity of feature C (and also of feature D in case of CeO_2) does not change with pressure, a clear pressure dependence is observed for the relative intensities of peaks A and B. As shown in Fig. 3, the relative intensity of peak A decreases with increasing pressure for both CeF_4 and CeO_2; our observation for CeO_2 is again inconsistent with a report of Röhler which claims no change in relative intensity with pressure.[2] An inspection of Figs. 1 and 2, however, clearly shows the de-

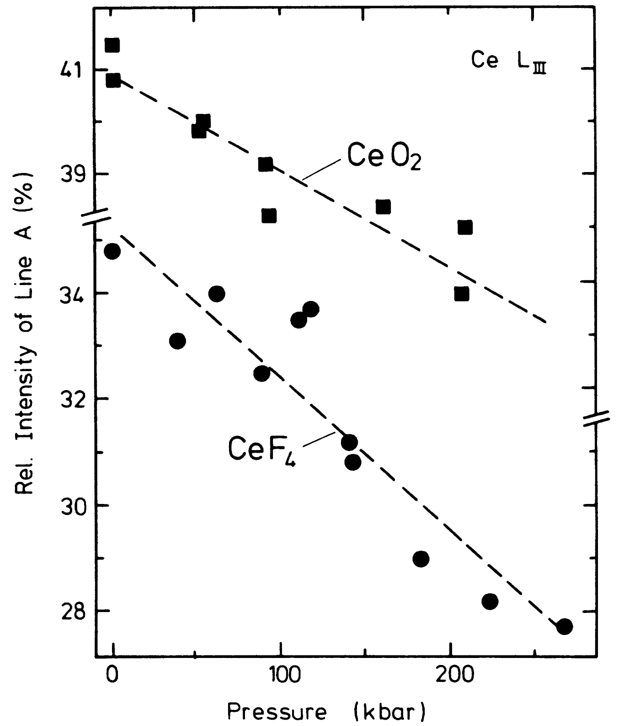

FIG. 3. Relative intensities of line A in the Ce L_{III} XANES spectra of CeO_2 and CeF_4 as a function of pressure.

crease in the weight of peak A with pressure. In addition to these pressure-induced intensity variations, we also found marginal increases with pressure in the energy separations of peaks A and B (~6.5 eV for CeF_4 and ~7.5 eV for CeO_2 at ambient pressure) amounting to ~0.3 eV in both cases at the highest pressure values reached. When discussing the pressure-induced variation in the relative intensities of peaks A and B, we first note that it is opposite to all observations made hitherto with mixed-valent metallic Ce compounds and also with other mixed-valent compounds of heavier RE elements.[2,16,17] If, as according to model (i), CeO_2 and CeF_4 are assumed to be mixed valent with localized $4f^0$ and $4f^1$ configurations mixed in the ground state [giving rise to subspectra A ($\underline{2p}4f^05d^*$) and B ($\underline{2p}4f^15d^*$)], the application of external pressure should favor the Ce configuration with the smaller ionic volume, i.e., Ce^{4+} $4f^0$, and hence cause an increase in the relative intensity of subspectrum A. This is indeed found to be the case in metallic mixed-valent Ce compounds,[2] while for both CeO_2 and CeF_4 clearly the opposite pressure effects are observed (see Fig. 3). This observation then strongly opposes models (i) and (ii) proposed for an interpretation of the L_{III} XANES spectra of formally tetravalent nonmetallic Ce compounds, while it is fully consistent with models of category (iii) which take covalency-related many-body effects due to the Coulomb attraction of the final-state core hole into account.[5,6,8,9] In these models, the L_{III} XANES spectra of formally tetravalent insulating Ce compounds reflect the degree of covalency between $4f$ electrons and ligand electrons in the ground state that is expected to increase with pressure. This in turn will cause the observed increase in the relative spectral weight of peak B, which—in the many-body framework—represents a mixture of $\underline{2p}4f^15d^*$ and $\underline{2p}4f^25d^*$ final-state configurations.

In summary, the results of the present high-pressure L_{III} XANES study of CeO_2 and CeF_4 are in full agreement with previous descriptions of these compounds in terms of tetravalent wide-gap insulators, with certain amounts of covalent admixture of $4f$ character into the ligand valence bands.[5-12] This picture is strongly supported by the results of band-structure calculations for CeO_2,[18] and also agrees with recent theoretical descriptions of L_{III} XANES spectra of CeO_2 and CeF_4 in the framework of the Anderson impurity model.[8,9] While the band-structure results reveal an extended radial character of the f partial waves covalently admixed into the filled ligand valence band,[18] the latter many-body calculations assume atomic character for these $4f$ states. Valence-band and shallow core-level photoemission results for CeF_4 (Ref. 5) as well as a previous bremsstrahlung-isochromat spectroscopy study of CeO_2 (Ref. 19), however, support the view of a more extended character of these covalently admixed $4f$ states. Therefore, a classification of CeO_2 and CeF_4 in terms of classical mixed-valent Ce compounds, which has been proposed on the basis of $4f$ admixture into the delocalized ligand bands,[8,9] appears inappropriate. The tetravalency of these covalent insulators is well described by the band-structure calculation[18] and is also reflected in high-energy spectroscopy results,[5-7,20] low-energy optical spectroscopy,[12] as well as in their ground-state properties.[21]

The authors acknowledge the expert help of the staff of HASYLAB/DESY. This work was supported by the Bundesminister für Forschung und Technologie, under Project No. 05-313AX-B2/TP4.

---

[*] Permanent address: Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Bombay 400 005, Maharasktra, India.

[1] E. E. Vainshtein, S. M. Blokhin, and Yu. B. Paderno, Sov. Phys. Solid State **6**, 2318 (1965).

[2] See e.g. J. Röhler, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, p. 453.

[3] E. V. Sampathkumaran, G. Kaindl, W. Krone, B. Perscheid, and R. Vijayaraghavan, Phys. Rev. Lett. **54**, 1067 (1985).

[4] G. Wortmann, W. Krone, E. V. Sampathkumaran, and G. Kaindl, Hyperfine Interact. **28**, 581 (1986).

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

[6] G. Kalkowski, G. Kaindl, G. Wortmann, D. Lentz, and S. Krause, Phys. Rev. B **37**, 1376 (1988).

[7] G. Schmiester, G. Kaindl, and P. Wachter, in *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions*, edited by L. C. Gupta and S. K. Malik (Plenum,

New York, 1987), p. 663.

[8] T. Jo and A. Kotani, Solid State Commun. **54**, 451 (1985).

[9] A. Kotani, K. Okada, and M. Okada, Solid State Commun. **64**, 1479 (1987).

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

[11] D. Wohlleben, J. Röhler, R. Pott, G. Neumann, and E. Holland-Moritz, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 143.

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

[13] J. E. Müller and J. W. Wilkins, Phys. Rev. B **29**, 4331 (1984).

[14] N. V. Troneva, I. D. Marchikova, and I. B. Borovskiy, Fiz. Met. Metalloved. **6**, 141 (1958).

[15] G. Schmiester, doctoral thesis, Fachbereich Physik, Freie Universität Berlin, 1987 (unpublished).

[16] J. Röhler, D. Wohlleben, G. Kaindl, and H. Balster, Phys. Rev. Lett. **49**, 65 (1982).

[17] K. Syassen, G. Wortmann, J. Feldhaus, K. H. Frank, and G. Kaindl, Phys. Rev. B **26**, 4745 (1982).

[18] D. D. Koelling, A. M. Boring, and J. H. Word, Solid State Commun. **47**, 227 (1983).

[19] E. Wuilloud, B. Delly, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. **53**, 202 (1984).

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

[21] P. Wachter, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 145.