Spectroscopic Evidence for Localized and Extended f-Symmetry States in CeO$_2$

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The occupied and empty electronic states of the insulator CeO$_2$ have been studied by high-energy spectroscopies. The outer-level spectra reveal empty localized $4f^1$ states within the band gap. The core-level spectra display different final-state populations of the $4f$ localized states which are well predicted by a many-body calculation taking into account the presence of f-symmetry admixture in the valence band. A mixed valence can be definitely excluded in CeO$_2$.

The electronic structure of Ce metal and its intermetallic compounds has been and continues to be a very fascinating research area offering the best accessible possibility to investigate the consequences of the degeneracy between extended states of a metallic band and an atomiclike localized $4f$ state. Obviously, this situation cannot be described as a conventional hybridization since, despite their strong interaction, these two kinds of states keep to a large extent their respective extended and localized character. The resulting many-body states seem to be correctly accounted for in the framework of the Anderson impurity model, and the computation of the response of such systems to very different spectroscopic excitations shows encouraging agreement with the experimental spectra.[1-3]

In an ionic compound like CeO$_2$, a new situation can be anticipated, which is different from the one met in Ce intermetallics studied so far. This fact is best demonstrated by the controversial opinions concerning the ground-state properties of this insulating compound. The observation of distinct $L_{\rm III}$ x-ray absorption edges of Ce has been interpreted as evidence of an initial $4f^0 \leftrightarrow 4f^1$ mixed-valent state.[4] However, this description has been called into question on the basis of optical and magnetic properties, reflecting the insulating character of this compound. A simpler picture of a formally full oxygen $2p$ band and a tetravalent ($4f^0$) configuration of the Ce atoms was proposed.[5] Later on a specific local valence-mixing mechanism between O $2p$ and Ce $4f$ states was attempted in order to reconcile mixed-valence behavior (deduced from core-level spectra) with the insulating properties of this material.[6] A very recent self-consistent-field band calculation of the electronic structure of CeO$_2$ indicates clearly that this compound is an insulator with a band gap of 6 eV.[7] A careful symmetry analysis of the ground-state eigenfunctions shows that the states of nearly pure $4f$ localized character remain

unoccupied ($n_f^l = 0$) in the band gap whereas the valence-band states contain a nonnegligible admixture of f symmetry ($n_f^b > 0$) with an extended radial behavior.[7] The aim of the present work is to test the compatibility of this ground-state description with the results obtained by different spectroscopies. A model calculation[1] taking into account the relevant aspects of this initial state has been performed in order to predict the different experimental spectra.

The spectra presented in this investigation were obtained in a spectrometer which allows us to perform x-ray photoelectron spectroscopy (XPS), bremsstrahlung isochromat spectroscopy (BIS), and electron energy-loss spectroscopy (EELS) on the same sample without breaking the base pressure of 1×10^{-11} Torr.[8,9] The CeO$_2$ sample was prepared *in situ* from metallic Ce films evaporated on graphite and oxidized at 800 K in an oxygen atmosphere of 1 Torr for 6 h. The check of the CeO$_2$ purity by monitoring the XPS O $1s$ signal yielded an upper limit of 5% for the presence of lower oxides. The electron bombardment of the surface in BIS and EELS was found to induce a fast surface reduction of CeO$_2$ to Ce$_2$O$_3$. This instability could be widely eliminated by exposing the sample to an oxygen atmosphere of 1×10^{-8} Torr[10] during the measurements. By varying the electron-beam current from 50 to 200 μA, no charging effect of the thin CeO$_2$ film could be detected. The outer-level energies in XPS and BIS spectra were calibrated with respect to the sample Fermi level determined within ± 0.1 eV by measuring a Au film deposited by evaporation onto CeO$_2$.

Figure 1 shows the occupied and empty density of states (DOS) of CeO$_2$ as obtained from the joined XPS and BIS spectra. Our XPS spectrum confirms an earlier result measured with a lower resolution on a pressed CeO$_2$ powder sample.[11] As far as we know, no BIS spectrum of pure CeO$_2$ has been published.[12] The agreement between the experimental spectra of Fig. 1 and the density of the

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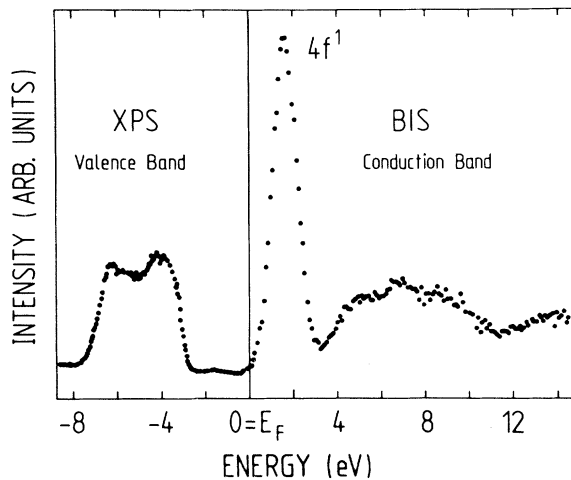
FIG. 1. Combined XPS-BIS spectrum of CeO_2.

ground-state eigenvalues shown in Fig. 2 of Ref. 7 is striking. The XPS valence band of mainly $2p$ character confirms the existence of many predicted fine structures. In the BIS spectrum, by extrapolation of the conduction band below the main peak, a band gap of ~ 6 eV is determined in good agreement with the calculation. The BIS spectrum displays also an upper edge delimiting probably an 8-eV-broad $6d$ band. The prominent peak located in the band gap represents unambiguously the single occupation of the initially empty $4f^0$ states. The measured full width at half maximum of 1.2 eV of this resonance is compatible with a $4f_{7/2,5/2}$ spin-orbit doublet convolved with two Gaussians of ~ 0.6 eV width representing the instrumental resolution and lifetime broadening.[13] This observation points out the localized character of these empty states. The position of the $4f^1$ excitation relative to the extended states is qualitatively in agreement with the computed position of the $4f$ state. However, for highly correlated $4f$ electrons the ground-state eigenvalues do not represent precisely the measured energies. From the spectra of samples containing a substantial mixture of CeO_2 and Ce_2O_3 we have clearly observed the XPS $4f^1$ and BIS $4f^2$ final states of Ce_2O_3 at -1.6 and 7 eV, respectively (barely discernible contributions can be recognized in the spectra of Fig. 1). It seems reasonable to assume similar screening mechanisms in the two oxides so that the $4f^1$-$4f^2$ energy separation is roughly the same in both cases. Thus, if there *were* any occupation of the local level, an additional $4f^2$ structure in the BIS spectrum would be expected at 10 eV, not far below the upper band edge; and if there were local f character in the valence band, additional structure would be expected near the lower
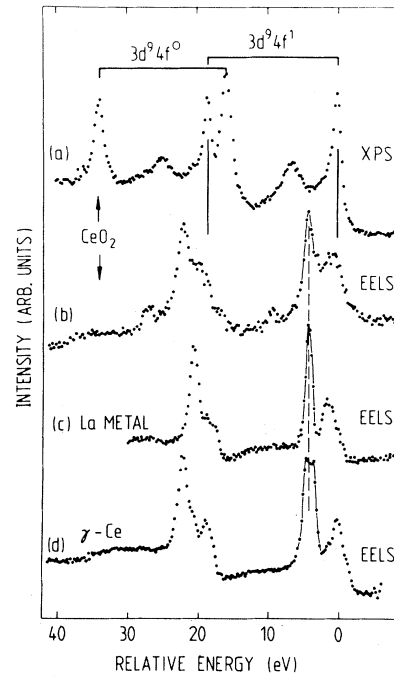
FIG. 2. (Curve *a*) XPS and (curve *b*) EELS spectra of $3d$ core excitations in CeO_2 on a common energy-loss scale. The spectra for (curve *c*) La and (curve *d*) γ-Ce are aligned.

conduction band edge. That no such $4f^2$ structures are observed attests to the fact that the local $4f$ states are completely unoccupied, in agreement with the ground-state calculation. The predicted existence of f mixing in the bands[7] cannot be directly recognized in the outer-level spectra but will be found to play an essential role in the coupling with the different core-hole final states.

The creation of a core hole destroys locally the translational symmetry by enhancing the potential of a particular atom. The extended band states are only weakly affected while the localized $4f$ states suffer an important lowering of their energy. The final states of any core-level spectroscopy will reflect a locally completely different situation than in the initial state around the ionized atom. Furthermore, in the sudden approximation, the existence of f character mixed to the initial valence-band states is considered responsible for a sizeable coupling to the different localized $4f$ final populations. For the moment, we shall only attempt to identify the different final-state configurations observed in the XPS and EELS spectra shown on a common energy scale in Fig. 2. In an insulator, the most natural way to define for XPS an energy scale compatible with the energy losses in EELS is to take the upper band edge as origin. The well separated

structures observed in the XPS $3d$ spectrum shown in Fig. 2, curve a confirm an earlier result obtained on a CeO_2 powder sample.[14] In the EELS spectrum of CeO_2, the two well separated spin-orbit–split components show the typical multiplet structures of a $3d^9 4f^1$ final state. This identification is established by comparison with the EELS spectra of La and Ce which have been shown to correspond to $3d^9 4f^1$ and $3d^9 4f^2$ final states, respectively.[9,13] These spectra are represented in Fig. 2, curves c and d with one of their leading peaks aligned on the corresponding peak of CeO_2 (dashed line). The data points of these peaks have been connected with a line to guide the eye in order to make conspicuous the differences between the EELS spectra of CeO_2, La, and Ce. A careful inspection of these multiplet structures shows that the CeO_2 EELS spectum is nearly identical to the one of the La and in fact different from the one of Ce. We can take advantage of the detailed analysis of the La spectra[9] and attribute in CeO_2 the XPS final state observed in the corresponding energy range to $3d^9 4f^1$ atomiclike final states. The nature of the weaker structures occurring at higher energies in XPS and EELS is not obvious but is likely to have a pronounced $3d^9 4f^2$ character.[6] Finally, the intense XPS lines at the highest energies can be identified with the $3d^9 4f^0$ final state, since no corresponding EELS structures can be found. This final-state identification based on experimental observations is at variance with the assignment made in the calculation of Thornton and Dempsey[15] but in agreement with the one of Ref. 6. It is interesting to notice that the weakest EELS structures were already detected in an earlier photoabsorption measurement[16] but could not be interpreted. Thus far we have been able to identify the nature of the different excitations observed in core-level spectra, but their relative intensity distribution cannot be simply predicted since the coupling between initial and final states must be calculated in a many-body formalism simulating the situation encountered in CeO_2.

We have adapted the Gunnaarsson-Schönhammer GS model[1] to the case of an insulator by defining a full valence band of rectangular shape allowed to hybridize with an f level above it. With the parameter values given in Fig. 3 the weight of the $4f^1$ configuration in the ground state is about 0.5, in qualititative agreement with the self-consistent field calculation.[7] Since the computed XPS and BIS spectra shown in Fig. 3(a) represent excitation spectra accounting only for f-symmetry states they cannot be directly compared with the ground-state calculation of the total DOS.[7] For the extended
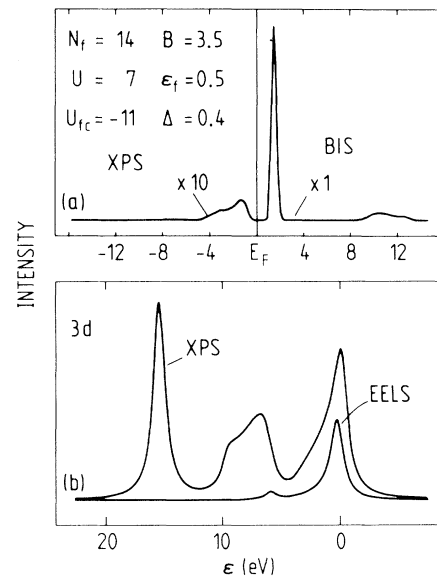

FIG. 3. Result of the many-body calculation for the different excitation spectra in CeO_2. (a) f contribution to the outer-level excitations. (b) $3d$ core excitations (see text). The spectra shown in (a) have been convoluted by a Gaussian of 0.4 eV full width at half maximum and those in (b) by a Lorentzian of 1.2 eV full width at half maximum. The parameters are defined as in Ref. 1.

states, however, the calculated f contribution to the exctitation spectra should be comparable to an f-projected DOS of a band calculation. As expected the f contribution in XPS is comparatively weak and broad. In the band gap the calculation predicts correctly the narrow resonance corresponding to the population of the localized $4f^1$ states. Since the model ignores the existence of a conduction band, instead of an f admixture to this band, it produces a rather unrealistic f^2 contribution. The same set of parameters producing excitation spectra of outer levels in good agreement with experiment has been used to calculate the core-level spectra shown in Fig. 3(b). The multiplet splitting which influences more strongly the EELS final-state structures has not been taken into account. With this simplification, the expected differences in the $3d \rightarrow 4f$ excitation processes between EELS and x-ray absorption spectroscopy, which are due to multiplet term-dependent matrix elements, have not been accounted for by the theory. In view of this omission and other approximations made in the model, it describes the XPS and EELS spectra surprisingly well. The calculated peaks in the XPS and EELS core-level spectra derive from the f^0, f^1, and f^2 final states in the limit of $V \rightarrow 0$ in the order of decreasing relative energy. However, at finite V, the

f^1, f^2 mixing impedes an unambiguous assignment. Finally, $2p \rightarrow 5d$ excitations (L_{III} edges), calculated within the same formalism, are in qualitative agreement with experiment.[4] The success of this formalism applied to the new situation encountered in CeO_2 provides a glaring demonstration that hybridized and extended f-symmetry states are also strongly coupled to deep-hole final states with different localized $4f$ populations.

This work has demonstrated that in CeO_2 the localized $4f$ states remain completely unoccupied whereas the proximity of the huge $4f$ resonance induces a nonnegligible $l = 3$ projected DOS in the valence band. These extended covalent states with f symmetry are responsible for the coupling to core-hole final states with different populations of localized $4f$ levels. This observation is confirmed by a model calculation describing the different spectroscopic processes, and it establishes quite generally that discrete final states in core-level spectroscopies do not necessarily reflect an initial mixed-valence state. The angular momentum rather than the degree of localization appears to be the essential parameter driving the coupling between the outer states when a core hole is suddenly created. It can be anticipated that this deepening of the core-level spectra interpretation will provide a powerful tool for probing the symmetry character of the states participating in the bond.

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