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X-ray absorption studies of CeO_2, PrO_2, and TbO_2.
II. Rare-earth valence state by L_{III} absorption edges

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The L_{III} absorption edges of fluorite-structure-related CeO_2, PrO_2, and TbO_2 show four well-resolved spectral features. The systematic trend in their positions and relative intensities suggests the presence of a specific valence state of the rare-earth atom in these oxides. The present study reveals an appreciable $4f$-$2p$ oxygen overlap in the valence band following the complete delocalization of the outermost $4f$ electron. Of the two main structures, the highest-energy one is interpreted as due to the localized $4f$ state and the additional presence of a hybridized $4f$ external state which we denote as $4\bar{f}$, is evidenced by the lower-energy peak. The weaker shoulder and preabsorptionlike feature are attributed to a shakedown effect due to the presence of an additional screening electron. This effect occurs both for the localized and for the extended orbitals of f symmetry, and a weaker structure therefore attaches to each of the strong peaks. The coexistence of localized and extended states is interpreted within a double-valley-potential model.

INTRODUCTION

Absorption spectroscopy at the L_{III} edge has proved to be an efficient tool for probing the valence of rare-earth atoms in different chemical environments.[1] In the present paper we argue that, for fluorite-structure-related RO_x ($R=$Ce,Pr,Tb; $1.5 \leq x \leq 2$) systems,[2] the oxygen environment determines whether the electron of dominant f character will be localized within the core or in an external state hybridized with the oxygen-derived valence band. A manifestation of this behavior is expected in the L_{III} ($2p \rightarrow 5d$) absorption transitions. In fact, the valence electrons are only involved in the final state of the $2p \rightarrow 5d$ transitions, and the spectrum yields useful information on the ground-state situation. Depending upon the $4f$-$2p$ oxygen hybridization, some weaker features due to the shakedown process are also expected. Our recent measurements on the $M_{IV,V}$ edges of these systems[3] (hereafter referred to as paper I) have demonstrated the presence of localized as well as extended states of f symmetry in RO_2. Although the identification of these two types of states is not so straightforward in L_{III} spectra, we will show that information on the $4f$ occupancy (n_f) at the rare-earth (RE) sites can be deduced.

Amongst the RO_2 systems, CeO_2 has been generally investigated[4-8] at the L_{III} edge in relation to the valence problem in Ce-based intermetallic compounds. At first sight, the analogy between the double-peaked L_{III} edge in CeO_2 and in the Ce intermetallic compounds leads one to believe that a similar valence transition mechanism is operating in both materials.[4] We attribute the similarity to hydridization of extended f states with the valence-band electrons. The consequence of such $4f$ hybridization may lead to the formation of spectroscopic final states in which it is difficult to characterize the spatial natures (localized or extended) of the resulting f-symmetry components. Under such circumstances the customary designation of the valence state by f^0, f^1, etc., and the notion of $4f$ occupancy (n_f) are only simplifications.[9] In such a situation, useful information on the spatial distribution of orbitals of predominantly f symmetry can be obtained from the spectral response of systems with additional corelike f electrons. In the context of materials containing Ce, such a situation occurs in their Pr intermetallic isomorphs and the fluorite-related RO_2. In the Pr intermetallic compounds, the observation of well-resolved complex features is difficult. Even for a dilute Pr impurity in Pd (Ref. 10) and in ZrB_{12} (Ref. 11), the valence of Pr deduced from L_{III} measurements remains close to 3. In this connection PrO_2 and TbO_2 seem to be the most promising candidates for such studies. So far, to our knowledge, no L_{III} measurements on TbO_2 have been reported in the literature. In the present paper we present a study of the L_{III} edge of CeO_2, PrO_2, and TbO_2 with the aim of deducing the RE valence state in these materials.

EXPERIMENTS AND RESULTS

The L_{III} absorption measurement were performed at Dispositif de Collision dans l'Igloo (DCI), Laboratoire pour l'Utilization du Rayonnement Electromagnétique (LURE), Orsay, which provides x radiation emitted by 1.72-GeV electrons in the storage ring. A silicon double monochromator (311) with a band pass of 2 eV was used to measure the absorption of the sample powders under atmospheric pressure. The L_{III} edges thus obtained from RO_2 powders are given in Fig. 1. These spectra are normalized to the absorption jump and presented in such way that the highest-energy main lines are aligned. We have also included in Fig. 1 the L_{III} edge from trivalent Tb_2O_3. The similar single-peak L_{III} spectra of Pr_2O_3 and Ce oxalate were also measured, but for brevity, are not reported here. The relative positions of various structures obtained from second-derivative spectra are given in Table I.

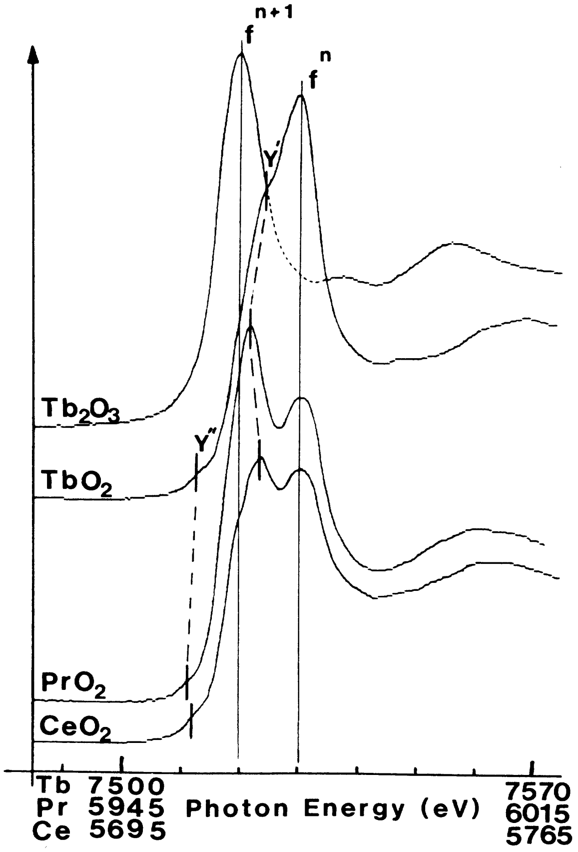

FIG. 1. The L_{III} absorption edges of fluorite-structure-related CeO_2, PrO_2, and TbO_2. For comparison, the L_{III} edge of Tb_2O_3 is included in the figure. The similar single-peak L_{III} edges of Pr_2O_3 and Ce oxalate are found to be aligned with the main peak of the Tb_2O_3. Within the experimental precision the weak shoulders are coincident with the trivalent L_{III} peaks.

TABLE I. Relative positions (in eV) of various structures obtained from the second derivative spectra; $n = 0$, 1, and 7, respectively, for Ce, Pr, and Tb in RO_2.

	Y''	f^{n+1}	Y'	f^n
CeO_2	-18	-12.2	-7.3	0
PrO_2	-18	-13.0	-9.7	0
TbO_2	-18	-11.2	-7.8	0

DISCUSSION

The main characteristic of the L_{III} edges of RO_2 is the systematic observation of two peaks of more or less comparable intensities. In TbO_2 the lower-energy peak (labeled Y') appears as a prominent shoulder. In PrO_2 it is slightly more intense than the high-energy peak. On the lower-energy side of the Y' structure we systematically observe in RO_2 a weaker shoulder (labeled f^{n+1}) at about 3 eV below the Y' structure. These weaker shoulders in RO_2 are observed to be coincident with the single line observed at the L_{III} edge of the corresponding trivalent oxide or compounds. In addition to the f^{n+1} shoulders we observe a preabsorption type of weak structure Y'' at about 10 eV below the Y' structure in CeO_2 and TbO_2. In PrO_2 it is found to be weaker and its presence was only detected in the second-derivative spectra of some samples.

Another characteristic of the L_{III} edges of RO_2 spectra is the systematic observation of two additional weak low-energy shoulders or structures (labeled f^{n+1} and Y'' in Fig. 1) beside the two main high-energy structures. This is in contrast to the trivalent oxides or compounds where a single line is observed at the L_{III} edge. However, the trivalent compounds of light RE elements show a weak low-energy shakedown shoulder 3–4 eV below the main absorption line.[12,13] The intensity of this shoulder decreased with increasing Z due to decreasing $4f$ valence-electron overlap with the core. In Nd compounds its intensity is found to be nearly negligible.[12] Thus the complexity of the L_{III}-edge structure of RO_2 as compared to that of trivalent R_2O_3 suggests that the delocalization mechanism of the $4f$ electron is not as simple as one might expect merely from the chemical valence of R in RO_2.

Our interpretation requires the coexistence of two types of $4f$ orbitals. Denote these as $4f$ (the usual, localized type) and a new kind of $4f$ orbital, denoted $4\bar{f}$, which resembles an extended state but actually coexists with the ground state as originally suggested for atoms of RE sequence by Band and Fomichev.[14]

In order to account for our experimental results, we postulate the existence of two distinct wells in the effective radial potential (including centrifugal terms) experienced by f electrons in CeO_2. Arguments for and against the existence of an outer well in a solid have been advanced in the literature and we can summarize the situation as follows.

(i) There is much spectroscopic evidence for the existence of double wells in atoms and some evidence for the reinforcement of the barrier between the two wells in certain molecular compounds of the same atoms.

(ii) It has been pointed out, on the basis of this analogy, that valence changes in certain solids (the γ-α transition in Ce) imply an energy difference which corresponds rather well to the energy required to move a Hartree-Fock $4f$ orbital from the outer to the inner valley of a double-valley potential.[15]

(iii) It has been speculated, on the basis of Thomas-Fermi calculations of the atom in a solid[16] that there can exist a double-well structure in the solid and that a coexistence of localized and diffuse f orbitals nearly degenerate in energy would explain the occurrence of intermediate valence.

(iv) Only two examples have been reported to date of an unresolved ambiguity in the self-consistent-field eigenfunction of a double well in a free atom or ion. These examples concern a $4f$ wave function in the Dirac-Fock model (Band and Fomichev[14]) and $5f$ wave function in the Hartree-Fock model (Connerade and Mansfield[17]). Only the former corresponds closely to intermediate valence as considered here, and Band and Fomichev claimed the possible coexistence of two solutions. For $4f$ electrons this seems to be a property of the Dirac-Fock model (i.e., a relativistic effect) and is the only (theoretical) example so far of "intermediate valence" for a free atom.

(v) It has also been argued that there is in fact no double-well structure for an atom in solid when treated by the Hartree-Fock model with a Wigner-Seitz boundary condition, and therefore that the conclusions of Schlüter and Varma[16] are due to artifacts of their calculation (Bringer[18]). One should note that Bringer's calculations are purely atomic within the Wigner-Seitz cell and that the Hartree-Fock method (as opposed to the Thomas-Fermi model) runs into difficulties in computing the density of states near the Fermi edge in a solid. Anyway, there are fundamental reasons why one does not expect any coexistence of different $4f$ states to be possible in Hartree-Fock as opposed to Dirac-Fock calculations.

In conclusion, the arguments which have been advanced in (i)–(v) are largely theoretical and are all open to objections on various grounds. In particular, if one argues as do Schlüter and Varma by analogy with the situation in atoms, then it seems to be a minimum requirement to start out from a relativistic model (which they have not done) since this is the only known case of the coexistence of different solutions for free atoms. Likewise, the Hartree-Fock model is probably not accurate enough in condensed matter to exclude the existence of the outer well or of some kind of barrier effect completely. Even if it were, the conclusion would not necessarily be relevant to CeO_2, in which one can also argue that the oxygen atoms, located at about 2.5 Å from the Ce atoms, introduce a molecular reinforcement of barrier which is not considered in any of the calculations.

This last possibility is probably the most relevant to our present study. We find that the single hypothesis of a double-well potential capable of supporting localized as well as diffuse f states can account for all our observations of the spectra of RO_2 (in which the R atom is surrounded by eight symmetrical oxygen nearest neighbors), whereas this hypothesis is not required to account for the spectra of trivalent oxides in which there are only six oxygen nearest neighbors and two vacancies. This very strongly suggests that the double-well potential is at least partly of molecular origin in RO_2 and that much of the theoretical controversy summarized above is only partially relevant to the physical problem considered here.

Nevertheless, there is one important aspect of all the theoretical papers in which $4f$ functions are calculated in a critical regime of a double-well potential. We note that the $4f$ orbitals all possess double maxima and in particular that the eigenfunction with maximum amplitude in the outer well always possesses a loop in the inner well and therefore a finite overlap with the core. Consequently, when we come to consider the states in RO_2 which we describe as external and which will be hybridized with the valence band, we expect that the external orbitals will also give rise to shakedown processes. These will not be weakened as compared with shakedown from localized states, since the balance of amplitude between the two wells depends on the degree of hybridization, to which the inner loop of the external orbital remains insensitive.

Finally, we remark that all the points we have made above concerning CeO_2 and trivalent oxides of Ce can be extended systematically down the sequence of rare earths R where $R=$Ce, Pr, and Tb. Thus, we expect systematic trends in the observation of supernumerary features in the spectra of RO_2.

From the discussion above, we expect two kinds of structures at the L_{III} edge of RO_2. This interpretation hinges on the change in the $2p$-$5d$ transition energy which is due to the variation in the core-hole screening by a spectator $4f$ electron and a $4f$ electron hybridized with the valence band. The main high-energy peak of RO_2 in Fig. 1 exhibits a clear multiplet structure. It appears only in RO_2 but not in trivalent oxides or compounds, consistently in agreement with the conclusion reached in paper I on the identification of the $3d^9 4f^{n+1}$ multiplets in the $M_{IV,V}$ spectra of RO_2. We assign it as f^n (f^0, f^1, and f^7, respectively, for Ce, Pr, and Tb in RO_2) ground state.[19]

The main low-energy peak labeled Y' (which appears as a prominant shoulder in TbO_2) in Fig. 1 we assign as transitions involving an external $4f$ state hybridized with the valence band.

The two features labeled f^{n+1} and Y'' in Fig. 1 attach to each of the main peaks, emulating their widths and general appearance. We describe them as shakedown peaks which, as described previously, are expected for both $4f$ and $4f$ electronic states. In the case of CeO_2 the separation between the f^0 line and the f^{n+1} shoulder is about 12 eV (Table I). This value is in good agreement with the separation (11 eV) between the $2p$-$5d$ excitation energy and the energy of the $4f$ electron-screened low-energy satellite estimated by Herbst and Wilkins[20] for tetravalent Ce. The calculations for tetravalent Pr and Tb are not available, but we expect these separations to be similar to those observed in tetravalent Ce.

Recently Jo and Kotani[21] proposed an elaborate theory of photoabsorption in CeO_2. They interpreted the L_{III} absorption spectrum of CeO_2 in the framework of the Anderson impurity model by taking into account the intra-atomic Coulomb interaction U_{fd} between a $4f$ electron and a photoexcited $5d$ electron. Through the investigation of the effect of U_{fd} they explained the difference in spectrum between the $3d$ x-ray photoemission spectroscopy (XPS) and the L_{III} edge structure of CeO_2. The calculated L_{III} spectrum, with the use of relevant parameters was found to reproduce the spacing (10 eV) between the two main peaks and their relative intensity of the observed L_{III} edge. However, they did not consider in their treatment the presence of a weaker feature which is situated at about 18 eV below the main highest-energy peak. Another proposal[22,23] using the Gunnarsson-Schönhammer[24] single-impurity approach considers the L_{III} edge features of certain rare-earth compounds as the $3d$ XPS lines convoluted with the $5d$ unoccupied density of states. This procedure is able to simulate well the L_{III} edge of CeCo_2. The results of such a comparison for CeO_2 were found to be less satisfactory.[22] From this discussion it appears that the difference between the 18-eV spacing observed between the two outer features in the L_{III} edge of CeO_2 and its reduced separation obtained by the impurity calculations needs some further theoretical attention. It is rather difficult to find a reasonable correspondence between the positions of the four structures observed in the L_{III} edge of $R\mathrm{O}_2$ and the three lines observed in $3d$ XPS of CeO_2.

By taking into account the absorption jumps (arctangent contributions), an estimate of the areas under the Y' and f^n peaks directly yields the spectral weights related to the occupied and unoccupied f states. We thus obtain an f occupancy (n_f) of about 0.5, 0.6, and 0.3, respectively, for CeO_2, PrO_2, and TbO_2. Our estimated values of n_f for CeO_2 and PrO_2 are in agreement with the band-structure calculations.[25] The impurity calculations on CeO_2 also yield a value of about 0.5 f electrons in the ground state.[21,22]

CONCLUSION

The L_{III} absorption edges of $R\mathrm{O}_2$ reveal systematic features attributed to a specific valence state of the RE atom in $R\mathrm{O}_2$. Four well-resolved structures are observed, which we interpret as two main peaks, due to transitions screened by localized and extended $4f$ states, and as two weaker shakedown satellites, one attaching to each of these main peaks. The presence of the four well-resolved structures, their detectable variation in the multiplet structure, and their systematic behavior as R is changed are quite readily understood within our model of a double-well potential with coexistent states. Other interpretations, based on the Anderson impurity model, do not lead so naturally to four structures of the type and the spacings we have observed. Clearly further theoretical work is required to establish whether variations in localization do occur, and what effect they have on the screening in L_{III} absorption spectra.

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