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**CeO<sub>2</sub> X-RAY RESONANT SPECTROSCOPY**

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RESUME: Différents échantillons de CeO<sub>2</sub> préparés sous diverses conditions expérimentales ont été analysés par photoabsorption X comparativement au Ce métallique.

Pour les échantillons sous stoechiométriques, les pics caractéristiques de la valence Ce<sup>3+</sup> sont largement dominants. Pour le dioxyde "pur" il n'y a pas d'électrons 4f localisés à l'état fondamental; des états étendus à caractère 4f sont observés confirmant ainsi la covalence partielle de la liaison dans ce composé

ABSTRACT: Various samples of CeO<sub>2</sub> prepared under different experimental conditions have been studied by X-ray photoabsorption comparatively to Ce metal.

For substoichiometric samples, peaks characteristic of the Ce<sup>3+</sup> ion are predominant. For "pure" dioxide the spectra reveal no localized 4f states are present in the ground state while extended states with 4f character are observed confirming partial covalency of bonding in CeO<sub>2</sub>.

## INTRODUCTION

The electronic structure of cerium in its various compounds is still a subject of controversy. In insulating compounds such as CeO<sub>2</sub>, with the chemists' view, Ce is tetravalent and no localized 4f states are present. On the other hand, on the basis of the mixed-valence point of view, a valence almost equal to three has been suggested for Ce in any chemical environment, corresponding to a ground state of 4f<sup>1</sup> configuration; this last argument was based on results obtained from XPS and L<sub>3</sub> photoabsorption spectroscopies.

Indeed several experimental results, in particular from optical (1) and bremsstrahlung isochromat (2) spectroscopies show the absence of localized 4f electron in CeO<sub>2</sub>. Among the techniques in which a core hole is present at the final state, the nd photoabsorption spectroscopy is the most convenient to determine the 4f configuration for two reasons: first, the coupling between the 3d hole and the unpaired 4f electrons dominates the fine structure which is thus sensitive to the number of 4f electrons. Second, no final state effect is present because the core hole is screened by the 4f excited electron, making these photoabsorption spectra well interpreted in terms of initial state effects. On the other hand, the 3d spectra are simpler than the 4d ones because the spin-orbit coupling is larger than the d-f interaction energy and multiplet structures are located under their own ionization threshold making autoionization negligible.

With this in mind, we have investigated the Ce3d absorption and emission spectra of Ce metal and CeO<sub>2</sub> in the aim to determine which spectral features allow to

identify the 4f configuration in the Ce compounds.

#### EXPERIMENTS

Conventional X-ray spectroscopy has been chosen to carry out the experiments; the continuous radiation emitted by a W anode was used for the photoabsorption measurements.

Pure Ce metal was obtained by thermal evaporation and covered with a thin Al film in order to avoid oxydation. Several oxydes have been prepared by different ways: pure Ce was evaporated and oxydized "in situ" in dry oxygen atmosphere (sample 1), CeO<sub>2</sub> powder of purity 99,9 was evaporated and either kept into vacuum and exposed to air for a short time before introduction in the spectrograph (sample 2), or exposed to air for a few hours before experience (sample 3), or reoxydized in dry air at 400 K for 15 hours (sample 4).

The samples were controlled by electron diffraction. The diagram obtained from pure powdered CeO<sub>2</sub> and those displayed by the different oxydes were all alike within the limits of the experimental precision.

#### RESULTS AND DISCUSSION

Figure 1 reports the 3d photoabsorption spectra for Ce metal and the four Ce oxyde samples. These latter spectra differ strongly according to the sample preparation. A close similarity is observed between the curves of Ce metal and samples 1 and 2; only a weak supplementary shoulder denoted by an arrow on the figure is noticeable on the oxyde curves. In contrast, the curves referring to samples 3 and 4 are drastically different. They exhibit two intense lines, denoted A and B, followed each one towards high spectral energies by a secondary peak. However a slight contribution at the position of the Ce metal peaks is observed for sample 3 which is not present in sample 4. Moreover, a very faint structure A' is present towards low energies from line A.

As it is well known, in the metal, the 3d spectrum exhibits multiplet structure which corresponds to the 3d<sup>9</sup>4f<sup>2</sup> final state showing the ground state configuration is 4f<sup>1</sup> (3).

On the other hand, to the 4f<sup>0</sup> ground state configuration corresponds a final state of 3d<sup>9</sup>4f<sup>1</sup> configuration. By analogy with the case of La, one expects in the 3d photoabsorption three lines, the two most intense ones corresponding to allowed dipole transitions towards the <sup>3</sup>D<sub>1</sub> and <sup>1</sup>P<sub>1</sub> levels. Indeed, for samples 3 and 4 the two main A and B absorption lines have the characteristics of transitions to such 3d<sup>9</sup>4f<sup>1</sup> final states.

The spectra from samples 1 and 2 are thus dominated by valence 3 features, only faint valence 4 contribution being present at the position of the main peaks A and B as pointed out by the arrows on figure 1. We suggest these samples are not stoichiometric. This is consistent with the fact that CeO<sub>2</sub> lattice can admit oxygen holes without change in lattice parameter (4).

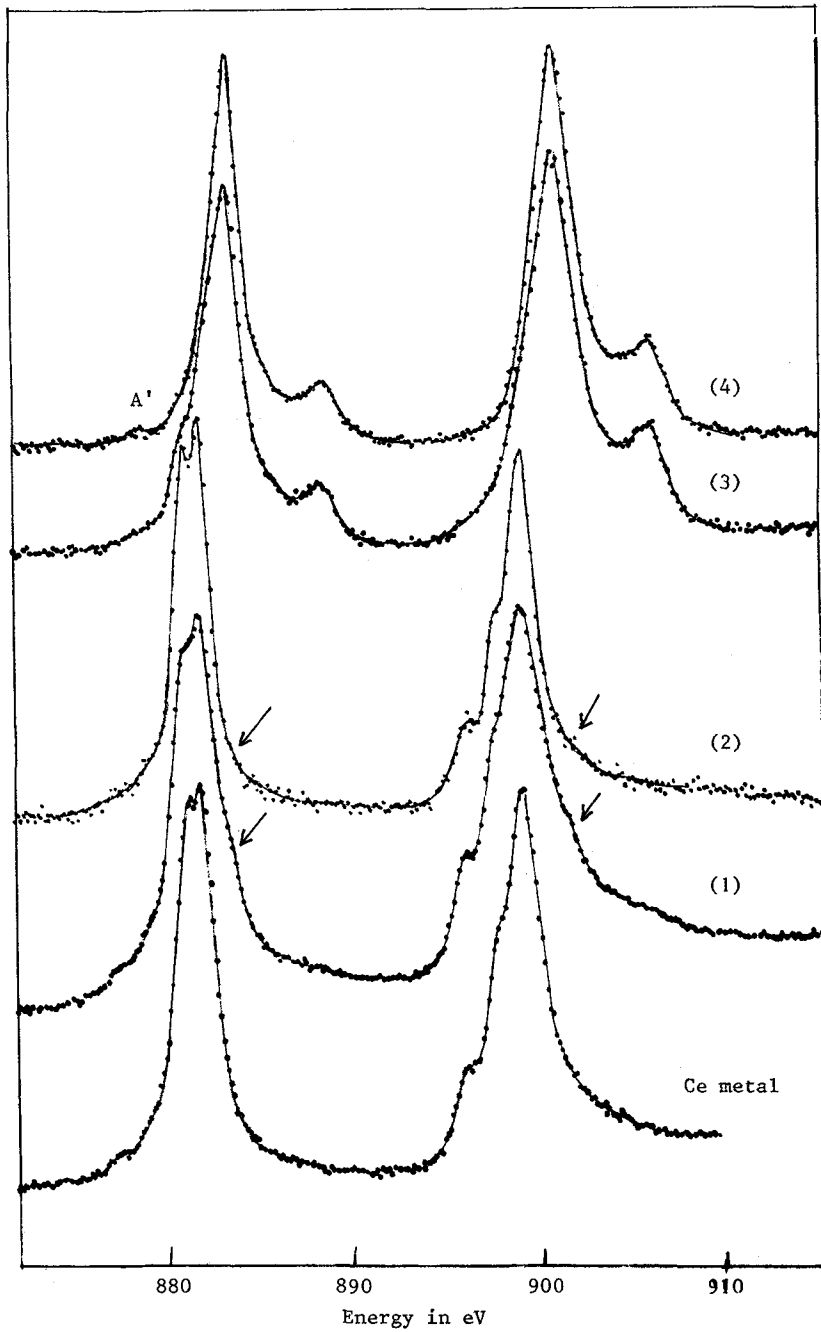


Figure 1: 3d photoabsorption spectra from Ce metal and Ce oxides

On the other hand, as suggested theoretically (5), the secondary peaks associated to A and B lines for samples 3 and 4 result from transitions to extended 4f-like states which are hybridized with Ce or ligand states of different symmetries.

Preliminary emission spectra reveal no essential difference whatever the sample. We do not ascribe an intrinsic origin to this result which we attribute to sample degradation under the electron beam due to the known instability of  $\text{CeO}_2$  compound (4).

In summary, our photoabsorption results ascertain that no localized 4f electrons exist in the ground state of  $\text{CeO}_2$ . Extended states with 4f character are present as theoretically predicted. These states remain delocalized in the presence of a core hole. Their observation agrees with the suggestion that bonding with partial covalent character exists in this compound. The experimental data obtained from optical spectroscopy (1), BIS (2), EELS (6), 4d photoabsorption spectroscopy (7,8) agree with this interpretation. Complementary studies are in progress in our laboratory in the aim to verify whether the data obtained from other spectroscopic techniques can also be interpreted in this model.

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