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Abstract. *In this work we have investigated the x-ray absorption spectra at the L₁ edge in formally tetravalent rare earth insulating materials which show mixing of many body final state configurations beyond single particle picture of XANES.*

1. Introduction

Excitations from 2s (L₁) core levels in rare earth atoms probe the local density of states of p-type bands or np (n>6) continuum states. The sensitivity of the L₁ spectroscopy to the valence state in these systems has been already qualitatively considered both in light and heavy rare earth [1,2] but no extensive investigation has been carried out if compared with the experimental data on L₃ edge. In the L₁ spectra of atomic rare earth, the threshold of the 2s→6p transition has been detected by Materlik et al. [3]. When the atoms undergo to a valence change going from the atomic phase to the metal phase, like in the cases of Sm and Er, a large shift of the order of 5 eV has been detected at the L₁ edge. We have measured the L₁ edge of rare earth atoms in several materials to investigate the nature of these chemical shift and in order to determine the valence state in insulating systems. In particular in the case of oxide materials with strong correlation effects, the L₁ edge spectra show the failure of the one-electron model to explain the experimental data.

2. Experimental

The experiment was performed at the Frascati Synchrotron radiation facility using the storage ring ADONE. The monochromator was equipped by a channel cut Si(111) crystal with a resolution of about 1.5 eV at the L₁ Ce edge. The samples was obtained spreading fine powders onto kapton scotch tape and measured in the transmission mode.

3. Results and Discussion

In fig.1 we report the L₁-XANES (X-ray Absorption Near Edge Structure) spectra of CeO₂, PrO₂ and TbO₂ which have the same crystal CaF₂ structure and therefore we expect similar one-electron features of unoccupied p states.[4,5] The differences are assigned to many body configuration interaction. The tetravalent rare earth oxides RO₂ are strongly

covalent oxides' where one-electron electronic band structure [4] shows mixing between the 4f orbitals and the oxygen 2p orbitals. The covalent character of the R-O bond is in competition with the high electronic correlation for the electrons in the 4f orbital such that the Coulomb repulsion U_{ff} is of the order of about 10 eV. The electronic correlation effects give in this case a specific electronic structure, classified as interatomic intermediate valence [6]. The gap in these correlated oxides is of the charge transfer type, determined by the energy separation ΔE between the $4f^n$ and the $4f^{n+1}\underline{L}$ configuration where \underline{L} indicates a hole in the oxygen derived band. The interatomic intermediate valent state is determined by the hybridization energy V between the 4f electrons and the oxygen 2p levels [7], when the condition $V > \Delta E$ is verified the $4f^n$ and the $4f^{n+1}\underline{L}$ configuration are strongly mixed.

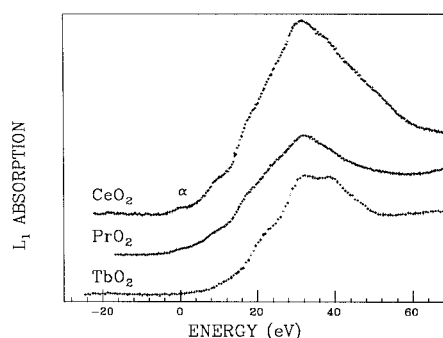


FIG.1 XAS spectra of Ce, Pr and Tb at the L_1 edge in the RO_2 oxides. The spectra are normalized in the XANES region and the zero of the energy scale has been fixed at the first weak absorption structure α .

In insulating Ce compound, for example CeO_2 , the experimental 3d-XPS (X-ray Photoemission Spectroscopy) has three peak structure [8,9] and the L_3 -XAS (X-ray Absorption Spectroscopy) has a two-peak structure [1,10]. The 4f final state configurations are different between the 3d-XPS and the L_3 -XAS, because in the absorption the Coulomb interactions U_{fd} (between 4f and 5d electrons) and $-U_{dc}$ (between 5d electrons and the core hole) play an essential important role in addition to the interaction $-U_{fc}$ (between 4f electrons and the core hole) which is almost the same for 3d and 2p core holes.

In fig.2 are reported the L_1 -XANES of cerium in four different compounds. These systems are insulators, but while the $Ce(PO_4)$ is a chemically trivalent system and at the L_3 edge exhibit a single white line, the others are formally tetravalent systems and shown the typical double structure at the L_3 edge. [1,11,12] The tetravalent spectra are characterized by a very broad maximum at about 12-14 eV to respect the maximum of the trivalent $Ce(PO_4)$ system and there is a very slow rise of the edge which in the case of CeO_2 start at the same energy of the trivalent cerium compound. It is important to underline that the shift of the absorption maxima observed at the L_1 edge of the correlated materials is not a "standard" chemical shift like reported for the atomic rare earths which undergoes to a valence change in the metal phase [3] but it is determined also by the mixing between the

final state configurations. Comparison in fig.2 shows that a shift between formally Ce^{3+} and Ce^{4+} systems is essentially determined by the $-U_{fc}$ term, while at the L_3 edge the shift between the $4f^0$ and the $4f^1$ configurations is given by $(-U_{fc}+U_{fd})$. At first approximation the U_{fp} term can be neglected at the L_1 threshold and in the approximation that the $-U_{fc}$ term is the same for a 2s and 3d core hole, the description of the L_1 absorption edge can be very similar to the 3d-XPS spectrum, with two or three electronic configuration with the same energy separation and intensity ratio as in the 3d-XPS.

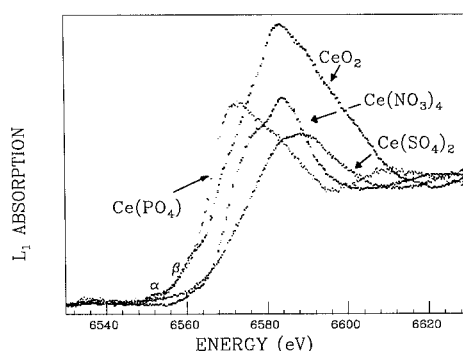


FIG.2 Ce L_1 edge in four different insulating systems. All the spectra are normalized in the region above the threshold.

The weaker shoulder α , β at the rising edge of the correlated insulator are directly related to the weights of $4f^{n+1}\underline{L}$ configuration in the final state, but the weight of the $4f^{n+1}\underline{L}$ contribution is weaker at the L_1 edge than in the L_3 , as a consequence that the intensity ratio between the two configurations decrease when their energy separation increase in the final state like at the L_1 edge.

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