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FINAL STATES AND INTERMEDIATE VALENCE IN XANES
OF INSULATING RARE EARTH OXIDES

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The XANES spectra of tetravalent rare earth compounds have been investigated. The L_3 , L_2 and L_1 edge spectra of CeO_2 , PrO_2 , TbO_2 and of cerium sulfate and nitrate have been measured. The edge spectra show multielectron final states that arise from configuration interaction in the ground state due to mixing of localized configurations $|4f^n\rangle$ and $|4f^{n+1}\underline{L}\rangle$.

These systems where the Hubbard correlation energy U_{ff} is larger than the charge transfer energy δE (which determines the separation between the two configurations in the ground state) are called interatomic intermediate valent systems⁽¹⁾. The variation of the energy δE and of hybridization determines the intermediate valence and the intensity and energy positions of final states in different samples.

Fig. 1 report the L_3 absorption spectra in CeO_2 , $Ce(SO_4)_2 \cdot 4H_2O$, PrO_2 and UO_2 . The spectra are normalized in the XANES region and the energy scales have been shifted to superimpose the EXAFS oscillations. The UO_2 , PrO_2 and CeO_2 have the same CaF_2 structure, which gives similar one-electron band structure^(2,3) and in fact valence band photoemission and BIS spectra of UO_2 and CeO_2 show many similarities. In particular all compounds have an eightfold oxygen coordination metal atom. The XANES are very similar as is shown in figure by the multiple scattering resonance at ≈ 40 eV beyond the threshold. Large differences appear in the low energy region, at threshold, in these insulating rare earths oxides and in spite of the very similar band structure and geometrical arrangement, CeO_2 , PrO_2 and $Ce(SO_4)_2 \cdot 4H_2O$ exhibit two strong features at the threshold with different intensity and energy separations. Moreover the multielectron final states show large differences at different edges. The 3d-XPS spectra of all studied compounds have been recorded and the comparison with XANES spectra is discussed.

We show that the configuration interaction between multi-electron final states is different at each edge and in XPS spectra. It is mainly controlled by the Coulomb interaction between the excited photoelectron with the valence 4f electrons which is different for each type of spectrum. Therefore the energy separation and mixing (therefore their intensity ratio) in the final states show large variations and only from a complete set of measurements the description of the ground state can be inferred.

Where $U_{ff} \partial E$, like in actinides⁽⁴⁾, only a single fully relaxed multielectron final state configuration is observed like in the case of UO_2 (see figure). In fact the L_3 spectrum of UO_2 shows a single atomic like resonance due to 2p-d transition to the empty d band above the Fermi energy which can be interpreted by one-electron transitions.

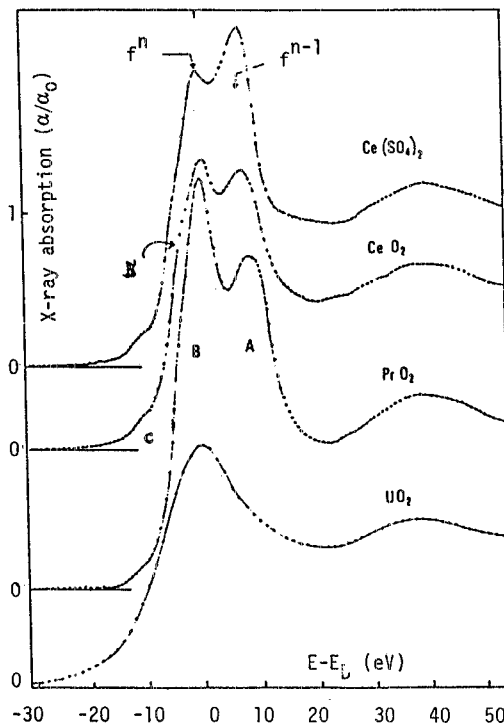


Fig. 1

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