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ABSTRACT

The Interatomic Intermediate Valence (IIV) state of f insulating compounds, has been detected by XANES (X-ray Absorption Near Edge Structure) in $Ce(SO_4)_2+4H_2O$, CeO_2 and PrO_2 but not in UO_2, formally $5f^2$ compound with the same CaF_2 structure and large f and ligand mixing. The multielectron final state configurations in XANES have been calculated with a many body theory both in the limit of a local cluster model and of a band structure. We show that the L_{III}-XANES is a good probe of IIV state and the description of these high correlated systems require a many body picture.

The unexpected presence of intermediate valence in insulating 4f compounds has attracted large interest because it seems to be a type of bonding at the edge between the localized and delocalized bonding. It is well known that both in lanthanides, actinides and transition metals, like cerium, uranium and nickel atoms it is possible to observe both localized and delocalized behaviour depending on the different chemical bounding. Here we have investigated Ce, Pr and U compounds which belong to this class of atoms. In the UO_2, PrO_2 and CeO_2 with CaF_2 structure and eightfold metal coordination evidence of large metal f and oxygen 2p mixing has been found both from band structure[1] and molecular orbital calculations for UO_8[2] and CeO_8[3] clusters. The XPS Ce(3d) core lines have been interpretated in terms of mixing of many body configurations for the local cluster CeO_8[4]. Evidence of a narrow unoccupied sharp band above the gap in BIS[5] of CeO_2 has been assigned to localized 4f states. A controversy has been raised concerning the interpretation of the data in terms of one electron band structure of crystal or many body configurations of a local cluster.

The Ce L_{III} absorption spectrum of CeO_2 remained an unresolved puzzle for many years since the first experiment[6-8]. In fact the L_{III} XANES (X-ray Absorption Near Edge Structure) of transition metals, actinides and lanthanides exibit a single white line at threshold which is due to a resonance in the $2p \rightarrow \epsilon d$ atomic cross section modified by a local density of unoccupied states[9]. This final states can be obtained by one electron theories[10].

Here we present a many body calculation of the repartition of the oscillator strenght of core $2p \rightarrow \epsilon d$ excitation in x-ray absorption which predicts the splitting of the white line and the lineshape of experimental features in the cases where the many body ground state description, because of localized configuration interaction, beyond the one-electron picture is required. This theory allows to obtain a picture of final states both in the limit of the local cluster model (N=1) as well as in the band structure limit (N=6).

We show that the interatomic intermediate valent state (IIV) in insulators is detected by XANES and the extracted valence of 4f occupation number is close to the ground state values. The presence of intermediate valence is mainly determined by the local chemical bonding but the extract value of the 4f occupation number in crystals is determined by the band structure. The interatomic intermediate valence in an insulating systems[11] is due to the mixing between f and ligand orbitals but this effect is not sufficient as it is shown here by the integer valent system UO_2 where there is a large mixing[2,12] but all hybridized orbitals are occupied[12,13]. This type of intermediate valence state is different from the well studied mixed valent state of metallic compounds.

The experiment has been performed on well characterized stochiometric samples both at the Frascati synchrotron radiation facility in LURE at Université Paris sud. Experimental details have been described elsewhere[14,15].

In Fig. 1 we report the L_{III} absorption spectra in UO_2, PrO_2, CeO_2 and $Ce(SO_4)_2 + 4H_2O$. The spectra are normalized in the XANEX 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 give similar one-electron band structure[1,12] and in fact valence band photoemission and BIS spectra of UO_2 and CeO_2 show many similarities[5,13]. In particular all compounds have an eightfold oxigen coordination metal atom. The XANES are very   similar as is shown in Fig. 1 by the multiple scattering resonance at ~ 40 eV beyond the threshold. Large differences appear in the low energy region, at threshold, in these compounds and only the UO_2 spectrum shows a single atomic like

FIG. 1 - XANEX spectra of Ce(So$_4$)$_2$+ 4H$_2$O, CeO$_2$, PrO$_2$ and UO$_2$ at the metal L$_{III}$ threshold.
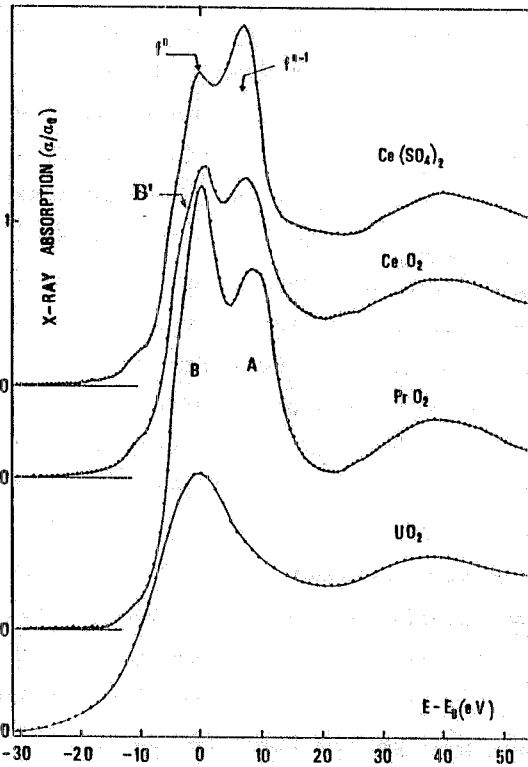
resonance due to 2p → ∈ d transition to the empty **d** band above the Fermi energy which can be explained by one-electron transitions. In spite of the very similar band structure and geometrical arrangement, CeO$_2$, PrO$_2$ and Ce(SO$_4$)$_2$+ 4H$_2$O exibith two strong features at the threshold with different intensity and energy separations.

In Fig. 2 we report the experimental results after subtraction of an arctangent function compared with curves obtained by fitting procedure. In the case of cerium compounds (lower part) we have fitted the spectrum with 4 lorentzians. The fitting procedure with 4 lorentzians is not enough to account for the details of the lineshape of the absorption peaks. In fact the lorentzian n. 3 has been introduced to account for a shoulder B' on the low energy side of the peak **B** of the peak **A** there is a shoulder that is not fitted with a simple lorentzians n. 1. Ce(SO$_4$)$_2$ shows more symmetric and sharp feature **A** and **B** which can be better fitted with lorentzian curves.
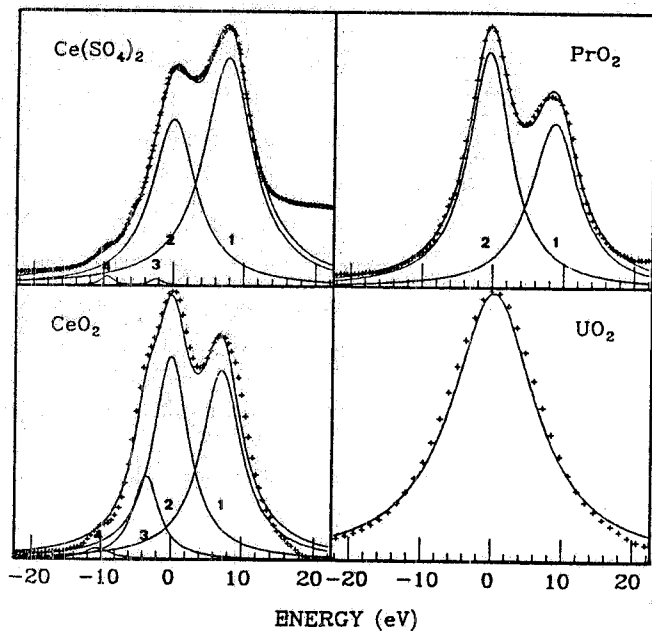
FIG. 2 - L$_{III}$ absorption threshold of studied samples after subtraction of an arctangent curve and the results of fitting with up to 4 lorentzians. In the case of cerium compounds the continuous line is the sum of the lorentzians 1,2 and 3.

In the case of UO_2 a single lorentzian is enough to give account for the main experimental feature but also in this case the fitting is not perfect. It is interesting to compare the spectra of $Ce(SO_4)_2$ and CeO_2. Long range solid state effects should be quite different in $Ce(SO_4)_2$ compound from CeO_2; on the contrary local electronic effects should be similar for the similar Ce coordinations. The XANES multiple scattering theory for a small cluster ErO_6 with a single shell around the metal atom[10] gives account of the main multiple scattering resonance at ~ 35 eV and for the $2p \rightarrow \varepsilon d$ transition at the threshold. In our case the experimental data show that the fine details of the features **A** and **B** in CeO_2 are due to solid state effects. The two experimental features **A** and **B** cannot be explained in the frame of single particle excitations. They are explained in the framework of many body theory. The ground state electronic structure of systems where there is a mixing between localized 4f levels and more delocalized ligand (O2p in our case) levels can be described by mixing of localized ionic multi-electron configurations: $4f^0$ and $4f^1 \underline{L}$ where $\underline{L}$ denotes a lignad hole.

This picture is considered a good approximation in insulating systems with localized molecular levels (i.e. with valence state with poor dispersion) as molecular systems like $Ce(SO_4)_2 + 4H_2O$ (in metallic systems with very delocalized bands this picture should not be appropriate). The two ionic configurations before hybridization are separated by δE. The hybridization between the atomic-like localized 4f and molecular-like delocalized O2p levels determines the mixing between the multielectronic configurations. The ground state is described by the wavefunction:

$$\psi_g = a|4f^0> + b|4f^1 \underline{L}>$$

Where **a** is not integer the system will be of mixed valent type. In the one-electron language the hybridization between the 4f and O2p determines a non-integer number of 4f electrons in the nearly pure localized 4f states. When these states are partially unoccupied the occupation number of the 4f electrons will not be integer. At threshold of x-ray absorption spectra in the final state there is a core hole in the metal atom and a photoelectron is excited in the first 5d unoccupied band. The L_{III} final state is determined by the Coulomb interaction Q_{hd} between the 5d electron and the core-hole, the Coulomb interaction Q_{hf} between the f electrons and the core-hole, and the Coulomb repultion U_{df} between the 5d and f electrons. As first pointed out by Kotani and Toyozawa because of the large Q_{hf} interaction the f states are deepen by the core-hole[16], but because of the Coulomb repultion U_{df} the f level are pushed up in the absorption. This last effect is the main difference between the XPS core final states and XAS final states[17,18]. The final states of intermediate valent Ce systems can be calculated, within the cluster model starting with a 4f level, a single (N=1) O2p orbital with a mixing parameter V between them, and a single unoccupied 5d orbital. Then the L_{III} edge spectrum $F_L(W)$ is expressed such that:

$$F_L(\omega) = \sum_f |<f|a_d^+|g>|^2 L(\omega + Eg - Ef)$$

$|g>$ (Eg) and $|f>$ (Ef) are respectively the eigenstate (eigenvalue) of the initial and final state of the hamiltonian, $(L(x) = \Gamma/\pi/(x^2 + \Gamma^2))$ and ω is the photon energy. Γ represents the spectral broadening due to the finite lifetime of the core-hole. a_d^+ denotes the creation operator of atomic Ce 5d orbital, where 2p core hole is produced. For details of these quantities, we refer to[17] and[19]. The band structure effects determines an oxygen 2p bandwidth in MO_2 (M=Ce, Pr and U) $W \sim 3$

eV[1,12]. To take account of this effect in the pratical calculation, we treat the valence band with energy ϵ_k as a finite system consisting of N discrete levels given by ϵ_k = -W/2+W/N(k-1/2) (k=1,...,N), where N valence band is taken as the origin of energy. The Ce 5d band is similarly replaced by N discrete levels with the band width 6 eV. Calculated spectra both for $F_L(w)$ are found to converge for N>4 and Γ= 1 eV. The results are plotted in Fig. 3. In the cluster (band) model, N=1 (N>1), the energy separation between the 4f level and the O2p level (center of O2p valence band) is assumed to be 1.6 eV which in the many body picture corresponds to the energy separation δE between $|4f^0>$ and $|4f^1 \underline{L}>$ configurations. The values U_{ff}= 10.5 eV and V=2 $\sqrt{2}$=2.8 eV have been assumed to describe the ground state. In fact E and V determines the non integer 4f occupation number or intermediate valence of the system. The energies Q_{hf}=-12.5 eV Q_{hd}=-6 eV and U_{df}=5 eV which are essential to describe the final state have been fixed.
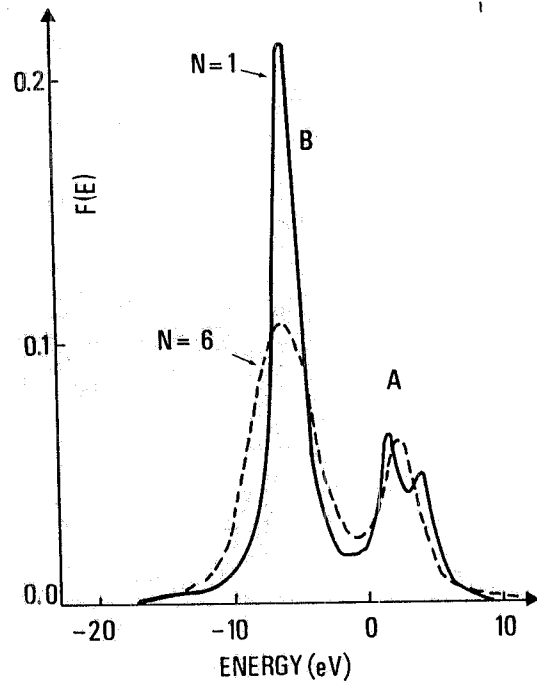

FIG. 3 - Calculated core absorption spectra for many body excitations with a 2p core hole and electron in 5d states, in the limit of the molecular cluster (N=1) and in the limit of finite width for filled valence and 5d bands (N=6).

In the final state we expect three configurations $4f^0$, $4f^1$ and $4f^2$. The energy separations in the cluster model (N=1) and V=0 are given by:

$$E(f^0)-E(f^1) = \delta F + Q_{hf} + U_{df}$$

and

$$E(f^0)-E(f^2) = 2(\delta E + Q_{hf} + U_{df}) + U_{ff}$$

The energy separation between $4f^0$ and $4f^1$ configurations in the actual calculation show in Fig. 3 is ~8 eV. The $4f^0$ and $4f^2$ configurations are very close and strongly mixed. In the case of N=1 with vanishing O2p and 5d bandwidth two features of the mixed $4f^0+4f^2$ configurations are observed. The effect of finite bandwidth determines a broadening of the $4f^1$ (low energy A feature) and the $4f^2$ final state but the effect is much larger on the $4f^2$ state which can not be anymore identified as a sharp spectral feature. The $4f^2$ configuration is pushed at high energy by U_{ff} and $2U_{fd}$ contributions therefore the low energy feature is mostly pure $4f^1$ and probes only the weight of the $|4f^1\underline{L}>$ configuration in the ground state.

Comparing these theoretical results with the spectra of $Ce(SO_4)_2$ and CeO_2 there is a good

agreement for the energy separation between the two multielectron final states. The experimental difference between the lineshapes of the two samples can be understood as due to the presence of an oxygen 2p band with 3 eV dispersion in CeO_2 and of localized O2p orbitals in $Ce(SO_4)_2$. In fact the feature **B** $(4f^1)$ in CeO_2 shows a broadening and a shoulder on its low energy side which is not present in $Ce(SO_4)_2$ as it is predicted by the theory. In fact using the lorentzian fitting it was necessary to add the lorentzian n. 3 to take account of this shoulder while it is nearly suppressed in the case of Ce $(SO_4)_2$.

The ratio **r** between the integrals of the oscillator strenghts of the experimental feature B/A+B can be used to measure the intermediate valence because the feature **B** is nearly pure $4f^1$ and the weight of the $4f^0$ configuration is distributed only in the experimental feature **A**. The parameters used in the theoretical model give a good agreement with the CeO_2 intermediate valence. The value B/A+B is obtained from the integrals of the lorentzians of the fitting, where the feature B is given by the sum of the lorentzian 2+3 and give 0,41, 0,54 and 0.56 for $Ce(SO_4)_2$, CeO_2 and PrO_2 respectively while UO_2 $(5f^2$ formal configuration) shows on the contrary a single final state configuration as integer valent systems.

In conclusion the classical mixed valent state or Intermediate Valent (IV) state of metallic systems arise from the interaction between $4f^n(5d6s)^{m+1} \longleftrightarrow 4f^{n+1}(5d6s)^m$ degenerate configurations ($\delta E=0$) with small hybridization on the contrary the IIV state of the insulating correlated (large U) systems arises from: 1) the mixing of $f^n \longleftrightarrow f^{n+1}\underline{L}$ configurations separated by $\delta E \neq 0$ 2) from hybridization $V \neq 0$ and 3) partially unoccupied f derived states.

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