A. Bianconi, I. Davoli, S. Della Longa, J. Garcia, K. B. Garg, A. Kotani, and A. Marcelli:
THE INTERATOMIC INTERMEDIATE VALENCE STATE OF INSULATING CORRELATED OXIDES CeO₂, PrO₂ AND TbO₂

Invited talk given at the Inter. Conf. on "Valence Fluctuations"
Bangalore India, (January 4-9 1987)
THE INTERATOMIC INTERMEDIATE VALENCE STATE OF INSULATING CORRELATED OXIDES CeO₂, PrO₂ AND TbO₂

A. Bianconi⁰, I. Davoli⁰, S. Della Longa⁰, J. Garcia⁰, K. B. Garg⁰*, A. Kotani⁵, A. Marcelli⁷

⁰Dipartimento di Fisica, Università di Roma La Sapienza, 00185 Roma, Italy
⁷Laboratori Nazionali di Frascati-INFN, P.O. Box 13, 00044 Frascati, Italy
⁵Department of Physics, Faculty of Science, Osaka University, Tojonaka 560, Japan
⁷Dipartimento di Matematica e Fisica, Università di Camerino, 62032 Camerino, Italy

I. - INTRODUCTION

The intermediate valence of formally tetravalent compounds has been detected by XANES (X-ray Absorption Near Edge Structure) in CeO₂, PrO₂ and in TbO₂ but not in ThO₂ and UO₂ which have the same CaF₂ structure. These materials, in the framework of many body theoretical description of the ground state by the filled-band Anderson impurity model, can be classified as interatomic intermediate valence (IV) systems whose specific properties are: i) a large mixing of 4f localized states with ligand valence orbitals, ii) a charge transfer energy δE (which determines the gap) smaller than the correlation energy U_{ff} (U_{ff}>δE) and iii) a hybridization energy V between 4f and oxygen 2p orbitals of the same order of magnitude as the energy separation ΔE between many body configuration 4f^n and 4f^{n+1}L, where L denotes a ligand hole (V~ΔE).

Permanent address:
*Department of Physics, University of Rajasthn, Jaipur, INDIA
*Departamento de Fisica de la Materia Condensata, Universidad de Zaragoza, Zaragoza, SPAIN
Here we report the results of an extensive investigation of these materials by L\textsubscript{1}-XANES, L\textsubscript{3}-XANES and 3d XPS (x-ray photoemission spectroscopy) and we discuss the different many body final states probed by each spectroscopy.

The Ce L\textsubscript{3}-XANES spectrum of CeO\textsubscript{2} has remained an unsolved puzzle for many years\textsuperscript{(1-5)}. In fact the L\textsubscript{3}-XANES spectra of actinides and lanthanides exhibit a single white line at threshold which is due to a resonance in the 2p->5d atomic cross section modified by local density of unoccupied states. This resonance can be obtained by one-electron theories\textsuperscript{(6)} both using multiple scattering approach of XANES in the real space\textsuperscript{(7)} as well as in the k space in the frame of band structure approach.\textsuperscript{(8)}

The spectrum of CeO\textsubscript{2} on the other hand, shows two white lines like the spectra of mixed valent Ce intermetallics. Here we show that like in CeO\textsubscript{2}, PrO\textsubscript{2} and TbO\textsubscript{2} L\textsubscript{3}-XANES also show two white lines while ThO\textsubscript{2} and UO\textsubscript{2} show the one-electron spectra at M\textsubscript{3} edge. We interpret the white line of L\textsubscript{3}-edge spectra by a many body calculation of the oscillator strength of the core 2p->5d excitations. The theory of the configuration interaction of the ground state of insulating oxides is required to obtain the many body final state. In CeO\textsubscript{2} by comparing the L\textsubscript{3}-XANES and the 3d-XPS spectra we observe the key role played by the Coulomb interaction U\textsubscript{df}=5 eV between the 5d photoelectron and the 4f electron.

The L\textsubscript{1}-XANES of correlated rare earth dioxides show many body features beyond the one-electron description of photoabsorption calculated by full multiple scattering schema (FMS).\textsuperscript{(9,10)}

2. - EXPERIMENTAL

The absorption experiment has been performed at the Frascati synchrotron radiation facility using the 1.5 Gev ADONE storage ring. Well characterized stochiometric samples were prepared by L. Albert and P. E. Caro at Laboratoire des Elements de Transition dans les Solids in Meudon (France).

XPS spectra have been measured by using a hemispherical electron analyser and the Al K\textsubscript{\alpha}-x ray emission line. Experimental details have been described elsewhere.\textsuperscript{(11,12)}

3. - RESULTS AND DISCUSSION

In Fig.1 we report the L\textsubscript{1}-XANES spectra of TbO\textsubscript{2}, PrO\textsubscript{2} and CeO\textsubscript{2}. The absorption coefficient has been normalized to the level of the atomic absorption jump at energies above the absorption edge. The zero of the energy scale has been fixed before the first weak absorption feature \(\alpha\).
The dashed curve reported in the lower part of the figure is an "ab initio" full multiple scattering (FMS) calculation of the L\textsubscript{1}-edge of cerium, including six shells around the absorbing cerium atom. Due to the lack of atomic resonances at the threshold of the 2s\rightarrow6p transition the spectral features are due to multiple scattering resonances of the excited photoelectron within the cluster. Qualitative comparison of this one-electron calculation with the experimental results shows the presence of the one-electron structure A and B in all spectra. TbO\textsubscript{2}, PrO\textsubscript{2} and CeO\textsubscript{2} have the same crystal structure and therefore we expect similar one-electron feature of unoccupied p states\textsuperscript{(13,14)}. The presence of the weak features α, β and C are assigned to many body final states not predicted by one-electron XANES theory.

In Fig. 2 we show the 3d\textsubscript{5/2} XPS spectra of CeO\textsubscript{2}, PrO\textsubscript{2} and TbO\textsubscript{2}. The spectra have been aligned to 3d\textsubscript{4}f\textsuperscript{0} configuration, and the energy scale gives the energy separation of different satellites from the main line. The satellite peaks B and C which appear in CeO\textsubscript{2}, have been interpreted by many body theories describing configuration interaction in the ground states\textsuperscript{(15-18)}. In the spectrum of CeO\textsubscript{2} we observe no features induced by Ce\textsuperscript{3+} impurities, which often appear in the Ce 3d-XPS spectra between the B and C peaks. This is an experimental evidence that in the samples there are no reduced cerium atoms. TbO\textsubscript{2} shows a single intense satellite separated by 11eV which we assign to 3d\textsubscript{4}f\textsuperscript{6}L\textsubscript{e} final state configuration, where L\textsubscript{e} denotes a ligand hole.
In Fig. 3 we report the L$_3$-XANES spectra of CeO$_2$, PrO$_2$ and TbO$_2$. The U and Th M$_3$-XANES in UO$_2$ and ThO$_2$ in Fig. 4 show at threshold a single white line due to a core transition to the unoccupied 6d orbitals enhanced by the resonance in the atomic absorption cross section for 3p$\rightarrow$6d transitions.

The presence of two white lines in CeO$_2$, PrO$_2$ and TbO$_2$ shows the breakdown of the one-electron description for core transition in these systems. The different peaks correspond to different final state configurations with different configurations of valence electrons.

The electronic structure of correlated insulating IIIV systems where there is a large mixing between localized 4f levels and more delocalized ligand (O 2p in our case) levels can be described by mixing of localized ionic multi-electron configurations: $4f^n$ and $4f^{n+1}L$.

The ground state is described by the wavefunction

$$\Psi_g = a \left| 4f^n > + b \left| 4f^{n+1}L > \right. \right.$$  

The two ionic configurations before hybridization are separated by $\Delta E$. The hybridization energy $V$ between the atomic-like localized 4f and delocalized O 2p states determines the mixing between the multielectron configurations. In the final states at the white line of L$_3$ XANES for IIIV systems the core hole is in the metal atom and the photoelectron is excited to the first 5d unoccupied band. The final state energies are determined by the Coulomb interaction $Q_{\text{vdW}}$ between the 5d electron and the core-hole, $Q_{\text{hf}}$ between the f electrons and the core-hole and the Coulomb repulsion $U_{\text{df}}$ between the 5d and the f electrons.
FIG. 3 - XANES spectra of CeO$_2$, PrO$_2$ and TbO$_2$ at metal L$_3$ threshold. The spectra have been aligned to 4f$^{n+1}$L$_n$ final state configurations.

FIG. 4 - M$_3$-XANES spectra of Th and U in formally tetravalent oxides with CaF$_2$ structure: ThO$_2$ and UO$_2$. The zero of the energy scale has been fixed to the maximum of both white lines.
As first pointed out by Kotani and Toyozawa\cite{19} because of the large $Q_{hf}$ interaction the f states are deepen by the core-hole in the XPS core final states. The L$_3$-XANES final states are different from XPS because the Coulomb repulsion $U_{df}$ pushes up the f levels giving a reduced effective relaxation energy $Q_{hf}$+$U_{df}$\cite{15,19,20}.

The fact that each core spectroscopy gives different final states with different energy separation and mixing of final state configurations is clearly shown by comparing Fig. 2 and Fig. 3.

The final states of II\_V systems can be calculated using the filled band impurity Anderson model\cite{17,20,21}. Within the cluster model a 4f level, a single (N=1) O 2p orbital with a mixing parameter V between them, and a single unoccupied 5d orbital are considered. The eigenstate, with the lowest energy $E_g$ which is assumed to be a singlet state, of the initial state Hamiltonian is denoted by $|g\rangle$ and the L$_3$ absorption final state at energy $E_f$ by $|f\rangle$. The calculations have been performed for the case of CeO$_2$. The band structure effects determine an oxygen 2p bandwith in MO$_2$ tetravalent oxides $W=3$eV.\cite{13,14,22,23}

To take account of this effect in the calculations we treat the valence band with energy $E^V_k$ as a finite system consisting of N discrete levels given by

$$
E^V_k = -W/2 + W/N(k-1/2) \quad (k=1, \ldots, N)
$$

where N is the valence band width and we put $W=3$ eV; the center of the valence band is taken as the origin of energy. The Ce 5d band is similarly replaced by N discrete levels with the bandwidth 6 eV. Therefore the N=1 model is similar to the Fujimori cluster model and by increasing N we obtain the band structure model. The calculated $F_I(\omega)$ spectra for increasing values of N are found to converge for N>4 and $\Gamma=1$eV. The energy separation between the 4f level and the O 2p level (center of the O 2p valence band) is assumed to be $\delta E=1.6$ eV. The values of $U_{ff}$=10.5 eV and V=2.8 eV are obtained from analysis of 3d XPS core spectrum.\cite{17,20}

These values of $\delta E$, V and $U_{ff}$ determine the interatomic intermediate valence in CeO$_2$ in the ground state giving non integer 4f count $n_f=0.46$.\cite{17,21}

In the final state of L$_3$-XANES for the excitation of a 2p core hole and a 5d photoelectron we expect for CeO$_2$ three configurations 4f$^0$, 4f$^1$ and 4f$^2$ separated approximately by:

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

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

We assign the many body features A and B of CeO$_2$ in Fig.3 to the 4f$^1$L$_3$ and 4f$^0$ configurations respectively. The interaction $Q_{hf}$ plays a key role in the final states of XPS spectra of 3d core lines. $Q_{sd}$ and $U_{df}$ are essential to describe the L$_3$-XANES final states. Here the value of $Q_{hf}=-12.5$ eV was determined from Ce(3d) XPS spectra as represented in ref. 17. The two quantities $Q_{sd}$ and $U_{df}$ were obtained as -6 eV and 5 eV, respectively, to reproduce the energy separation and relative
intensity of experimental peaks A and B in L₃ absorption spectra of CeO₂. The results of the many body calculations are plotted in Fig.5a for the cluster model N=1 and for the band model N=6. The energy separation between 4f⁰ and 4f¹L₄ configurations in the calculations is in good agreement with the energy separations of the white lines in CeO₂.

In Fig.5b we report the spectra of CeO₂ and cerium sulfate (Ce(SO₄)₂+4H₂O) which have similar cerium oxygen distance in the same site geometry. The large variation of intensities and lineshape of the peaks A and B appear clearly. Comparing the spectra of cerium sulfate we can see the effects due to different crystal structure for similar local structure. The sharpening of the A and B features in cerium sulfate is in qualitative agreement with the theoretical predictions shown in Fig.5a for the decreasing of the dispersion of the O 2p band going from CeO₂ to cerium sulfate.

**FIG. 5** - a) Calculated core absorption spectra in the framework of filled band Anderson model for many body excitations with a 2p core hole and one electron in 5d states both in the limit of molecular cluster (N=1, solid lines) and in the limit of finite width (W=3eV) for filled valence and 5d bands (N=6, dashed lines). The theoretical parameters for calculation of the final states are Uₙ₁=5eV, Qₑ=12.5eV and Qₙd=6eV. The sharpening of the final states in the cluster limit is found.

b) L₃ absorption spectra of Ce in CeO₂ (solid lines) and Ce(SO₄)₂+4H₂O (dotted line).

In the L₁-XANES spectra we have shown that the final state is determined by photoelectron multiple scattering resonances where the wavefunctions of the photoelectron is delocalized on a large cluster of about six shells around the photoabsorber. Therefore the Coulomb interaction between the p photoelectron in the continuum and the f electrons (Uₚf) is expected to be smaller or negligible in comparison with Uₙ₁ present in the atomic transition at the L₃ white lines. In fact the
L₁-XANES of Ce and Pr in CeO₂ and PrO₂ can be deconvoluted in three one-electron components with energy separation and intensity ratio as in 3d-XPS spectra. This shows that \( U_{pf} \) in L₁-XANES generally can be neglected. We are now working to obtain a description of the final state in L₁ and L₃-XANES and in core level XPS spectroscopy for each oxides, starting with the same parameters describing the many body configuration in the ground state.

4. CONCLUSION

L₃-XANES and core level XPS are complementary methods for the determination of ground state properties of IIIV systems. In fact in the final state of the 3d-XPS spectroscopy of CeO₂ we have a different situation because the \( 4f^{n+1}L_{\pi} \) is mixed with the \( 4f^{n+2}L_{\pi}^2 \) configuration and well separated from \( 4f^n \) configuration.\(^{17,24}\) On the contrary in L₃-XANES the \( 4f^{n+2}L_{\pi}^2 \) configuration in the final state is pushed at higher energy by \( U_{ff} \) and \( U_{df} \) contribution and therefore the low energy feature B is the mostly pure \( 4f^{n+1}L_{\pi} \) configuration.

In conclusion the presence of the high binding energy line in XPS gives direct evidence of \( 4f^n \) configuration in the ground state while in L₃-XANES the low energy feature B gives a direct weight of the configuration \( 4f^{n+1}L_{\pi} \) in the ground state. Therefore comparing the experimental results for CeO₂, PrO₂, TbO₂ and cerium sulfate we conclude that in these materials the probability of occupation of \( 4f^{n+1}L_{\pi} \) configuration in the ground state is different from zero. Moreover the final state indicated by B in L₃-XANES for IIIV material cannot be assigned to charge transfer final state shake-up satellites because it has been shown \(^{(5,11)}\) that these satellites are strongly quenched in L₃ absorption.
REFERENCES