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A. Balzarotti, F. Comin, L. Incoccia, S. Mobilio, M. Piacentini
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K-EDGE ABSORPTION OF TITANIUM IN THE PEROVSKITES SrTiO_3 , BaTiO_3 AND IN TiO_2

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ABSTRACT: The X-ray absorption at the K-edge of titanium in cubic perovskites BaTiO_3 , SrTiO_3 and in TiO_2 (rutile) has been measured using synchrotron radiation. A detailed analysis of the fine structure components requires a description in terms of crystalline density of conduction-band states rather than a localized molecular cluster approach. Experimental values for the diatomic transfer integrals ($pd\sigma$), ($pd\pi$) and ($sd\sigma$) and for the average Ti 3d bandwidths are derived and compared with theoretical estimates. The d orbitals of alkali-earth ions are found to contribute to the upper bands well above the t_{2g} - e_g conduction bands. The effect of the finite photon momentum on the transition probability is briefly discussed.

In this letter we report on measurements of the absorption coefficient around the K edge of titanium in the perovskites ferroelectric BaTiO_3 (in the tetragonal phase) and SrTiO_3 (in the cubic phase) as well as in TiO_2 (rutile). We find that a simple molecular-orbital (MO) approach for the $(\text{TiO}_6)^{8-}$ cluster is inadequate to give an accurate description of the final excited electronic states. Instead this is provided by a detailed calculation of the one-electron density of states (DOS). In agreement with augmented-plane-wave (APW) calculations by Mattheis for SrTiO_3 ⁽¹⁾ the strontium 4d (and, presumably, the barium 5d) bands are found to be necessary to interpret the experimental spectra at energies far from the titanium edge.

In the transition-metal perovskites of the ABO_3 type as well as in rutile each Ti^+ ion is octahedrally coordinated by six oxygen atoms which produce a cubic ligand field. Actually these octahedra are slightly distorted, particularly in the ferroelectric phase of BaTiO_3 ⁽²⁾, but the amount

of this distortion is such that it can be safely neglected. The crystal field acting at the Ti site causes a splitting of the fivefold degenerate 3d states into a threshold t_{2g} and a twofold e_g level. The first band calculations performed with the LCAO (linear combination of atomic orbitals) method by Kahn and Leyendecker (KL) on SrTiO_3 ⁽³⁾, predicted empty d conduction bands derived primarily from these orbitals and evaluated a total electrostatic splitting at Γ of 0.62 eV, while a larger splitting of 2.4 eV due to covalency effects was anticipated. Subsequent work by Soules et al.⁽⁴⁾, Mattheis⁽¹⁾, Wolfram et al.⁽⁵⁾ and, more recently, by Pertosa and Michel-Calendini⁽⁶⁾ confirmed the results of KL on the symmetry of the lowest conduction-band states. Mattheis⁽⁷⁾ also discussed the relation between MOs and LCAO splitting and showed that the $e_g - t_{2g}$ crystal field splitting Δ for an octahedral isolated transition-metal complex is associated with the average e_g and t_{2g} band energies and not with the energy separation at Γ .

The upper empty levels associated with Sr and Ba atoms are believed to produce bands far removed from the energy gap whose position can be estimated from the appropriate ionization energies and Madelung potentials of these levels. Both these terms are dependent upon the ionic charge of the ions at the lattice sites^(8,9). Attempts were made to estimate the position of the Sr and Ti s-p conduction-band states in SrTiO_3 by KL⁽³⁾. Soules et al.⁽⁴⁾ place these bands well above the lowest 3d bands while Mattheis⁽¹⁾ finds that these bands and the strontium 4d bands nearly overlap the titanium e_g bands. More recently an empirical MO model was applied to TiO_2 , SrTiO_3 and BaTiO_3 by using a restricted set of basis functions including 3d, 4s and 4p metal-ion orbitals and 2p and 2s oxygen orbitals⁽¹⁰⁾. By fitting the LCAO parameters to the energies of the cluster states of rutile computed by Tossel et al.⁽¹¹⁾, Wolfram et al.⁽¹⁰⁾ calculate a set of parameters in good agreement with those given by Mattheis⁽¹⁾.

Experimentally only indirect information on the excited levels of the perovskites is available from the dielectric constant ϵ_2 derived from optical reflectance data^(12,13). The X-ray spectra of rutile measured on the K-edge of titanium were obtained with poor resolution^(14,15).

The experiments were performed at the Synchrotron Radiation Facility PULS at the Frascati Laboratories, using the Adone storage ring operating at its maximum energy of 1.5 GeV and at an average current of 50 mA. The radiation was transmitted through a thin Be window (70 μ thick) mounted in front of the entrance slit of a Si (220) channel-cut single crystal monochromator. The average resolution around 5 keV was better than 1 eV. Data were collected by a step scanning method at energy steps typically of 0.1 eV. The rotation angles of the goniometer satisfying the Bragg condition were read by a shaft encoder which in turn provides the absolute angular setting.

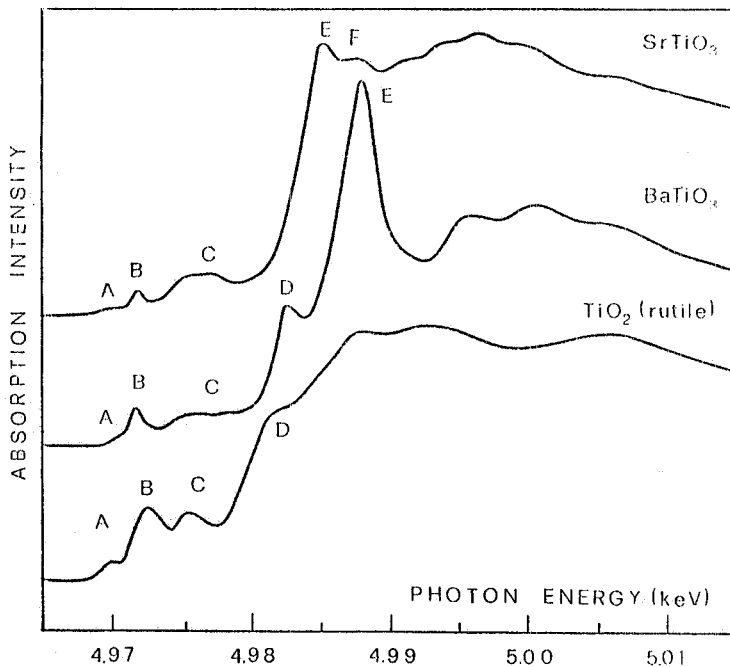


FIG. 1 - Absorption spectra near the K-edge of titanium.

The energy was calibrated by measuring the K-edges of several metals in the 4-12 keV range. The details of the experimental set-up will be described elsewhere. The samples were powder films layered on kapton tape obtained by grinding bulk single crystals. BaTiO_3 powder supplied by Merck Co. was also used to prepare the films, whose thicknesses were in the range $ud = 2$. Data acquisition and processing were done by means of an on-line computer PDP 11/03 which also controls the entire apparatus.

The Ti K-edge region of the three compounds is shown in Fig. 1. It can be seen that the correspondence among the structures labeled with the same letter is only qualitative, suggesting that final state effects contribute differently in these compounds. In fact peak C, which is sharp in rutile, broadens more than 5 eV in titanates and the struc

ture E in BaTiO₃ and SrTiO₃ is strong in comparison with the one in titanium dioxide.

In TiO₂ the lowest weak features A-B and C are ascribed to quadrupole transitions to empty antibonding states of d-like symmetry t_{2g} and e_g, respectively^(14, 15). The B-C splitting (2.9 eV) agrees well with that measured from the L_{III} and K absorption of Ti and from the K absorption of oxygen⁽¹⁴⁾. It can be rather well reproduced by a MO-LCAO calculation applied to the TiO₆ cluster. If only metal-oxygen and oxygen-oxygen interactions are included, the energy of a given cluster state is easily expressed in terms of two-center overlap and transfer integrals and of appropriate energy parameters related to the diagonal elements of the LCAO matrix⁽¹⁰⁾. We have estimated a value of 3.1 eV for the t_{2g} - e_g splitting using the parameters reported by Wolfram et al.⁽¹⁰⁾ who adopt the same Madelung potential as calculated for the perovskites and neglect overlap integrals. The strongest interactions are those between the 3d electrons of Ti and the 2p and 2s electrons of the six ligands which involve the two-center transfer integrals (pdσ), (pdπ) and (sdσ).

According to the cluster model^(10, 11), we ascribe the D peak of rutile to transitions to the 7a_{1g} and 7t_{1u} states derived from the titanium 4s and 4p orbitals, respectively. These states are separated less than 1 eV and thus the dipole-allowed 1s → 7t_{1u} transition dominates the weaker quadrupole 1s → 7a_{1g} transition. The present assignment reconciles both Fischer's⁽¹⁴⁾ and Tsutsumi's et al.⁽¹⁵⁾ conflicting proposals for the origin of the peak D.

Unlike titanium oxide, the absorption spectra of perovskites (Fig. 1) begin with a prominent peak followed by a nearly flat region composed of two very weak structures. The total bandwidth A-C is approximately 8.5 eV in SrTiO₃ and 9.5 eV in BaTiO₃, much larger than the average e_g - t_{2g} splitting of TiO₂. These features can be explained by considering the effect of the lattice periodicity on the crystal-field levels of an isolated complex. According to Mattheis⁽⁷⁾ the average e_g - t_{2g} separation is derived directly from the values of the energy-bands of the perovskites at the Γ and R points of the Brillouin zone, namely

$$\Delta = 1/2 [E(\Gamma_{12}) + E(R_{12}) - E(\Gamma_{25'}) - E(R_{25'})] . \quad (1)$$

Δ is exactly the crystal field splitting for an isolated octahedral complex which, to second order, is given by the expression⁽¹⁷⁾:

$$\Delta = e_g - t_{2g} + 1/2(\Delta_s + \Delta_\sigma - \Delta_\pi) , \quad (2)$$

where Δ_s, Δ_σ and Δ_π are parameters involving (sdσ), (pdσ), and (pdπ). The correlation between cluster and band states at these high-symmetry points results from the symmetry O_h of the k vector at both Γ and R points of the Brillouin zone. The wavevector dependence of the metal-ligand π and σ interactions broadens the t_{2g} and e_g levels into bands of width Δ_π and (Δ_σ - Δ_s) respectively, and shifts e_g by Δ_s, as depicted in Fig. 2. Consequently a measure of the bandwidth of the

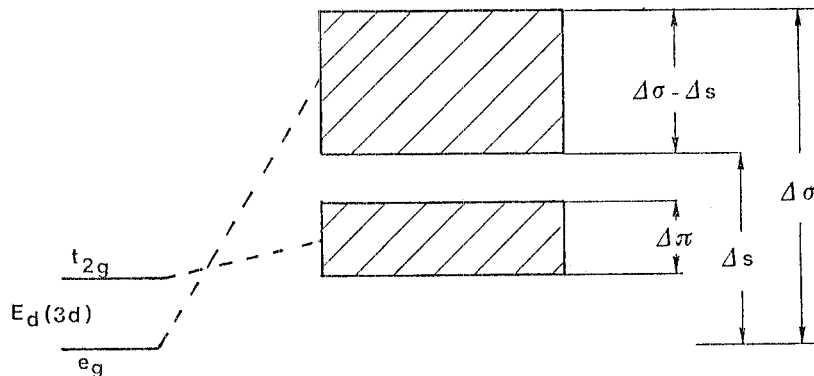


FIG. 2 - Simplified diagram of the crystal-field interactions on the 3d conduction levels of the perovskites.

A-B and C bands and of their average position provides an estimate of the metal-ligand interactions, provided the overlap integrals are known. We have used the overlap integrals (S_σ , S_π and S_σ') reported by Pertosa and Michel-Calendini⁽⁶⁾, which give apparently the best agreement with the experimental bandwidths for both compounds, to calculate transfer integrals. In Table I we compare our experimental values of the above parameters for SrTiO_3 and BaTiO_3 with theoretical estimates. In the calculations from Ref. (1, 3, 4, 5) reported in Table I the average $t_{2g} - e_g$

TABLE I - Comparison between theoretical and experimental values of some LCAO parameters in SrTiO_3 and BaTiO_3 . Energies are in Rydbergs.

Parameter	Mattheis (Ref. 1)	WKM (Ref. 5)	SKVR (Ref. 4)	KL (Ref. 3)	PMC (Ref. 6)	Present results
SrTiO_3						
($sd\sigma$)	- 0.1881	- 0.353	- 0.1881	- 0.253
($pd\sigma$)	- 0.1656	- 0.1639	- 0.308	0.1544	- 0.1656	- 0.146
($pd\pi$)	0.0835	0.0983	0.163	0.0618	0.0835	0.068
Δ	0.19	0.21	0.17	0.18	0.32	0.37
BaTiO_3						
($sd\sigma$)	- 0.2660	- 0.372
($pd\sigma$)	- 0.2754	- 0.252
($pd\pi$)	0.1382	0.135
Δ	0.41	0.43

splitting in SrTiO_3 is consistently smaller than the experimental one, indicating that the p-d overlap was underestimated. The p-d hybridization is particularly strong for the e_g band whose width is controlled by the ($pd\sigma$) integrals. The results of the "adjusted" APW calculations performed by Mattheis⁽¹⁾ for the conduction bands of strontium titanate are reported in Fig. 3.

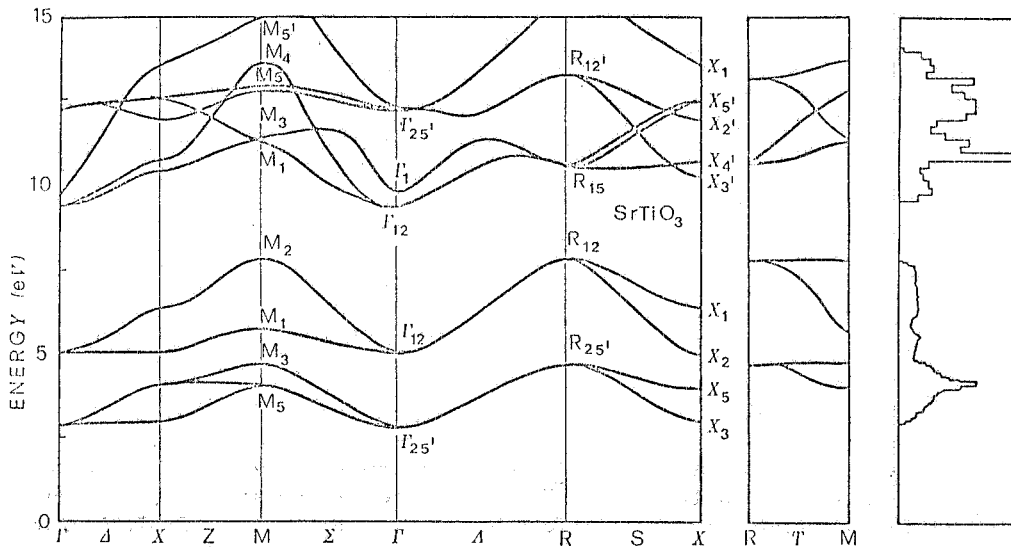


FIG. 3 - Adjusted LCAO conduction-band structure and density of states for SrTiO_3 according to Mattheis⁽¹⁾.

The DOSs of the various bands are shown to the right. The lowest portion of the DOS curve reproduces the original sampling of the Brillouin zone, while the upper one is obtained from the plotted bands and it should therefore be regarded as qualitative. A glance to Fig. 3 suffices to note the similarity between the DOS and the region A-C in Fig. 1. As it is well known, the absorption coefficient in the X-ray region is proportional to the density of the conduction band states, if the interband matrix elements are constant. This DOS is rather typical of cubic perovskites⁽¹⁾ and of ReO_3 ⁽¹⁸⁾, a compound having a crystal structure similar to that of the ABO_3 perovskites. The large narrow peak of the t_{2g} band results from the X_5-M_5 degeneracy, while the adjacent e_g broad band contains weak structures derived from the critical points at the points M_1 and X_1 . The over-all bandwidth is $0.3678 \text{ Ry}^{(1)}$, roughly half as large as that computed by Pertosa and Michel-Calendini⁽⁶⁾.

According to Mattheis⁽¹⁾, the additional conduction bands at higher energies include the antibonding 4s and 4p states of Ti and the d states of the A-atom. In the isolated Sr^{++} ion the 4d level is empty whereas in the crystal it forms two rather narrow bands which overlap the s-p bands. On the contrary the antibonding (s-p) bands are diffuse and their contribution to the DOS is fairly weak. So the rise of the absorption marks the transitions to s-p bands at Γ_1 and the strongest doublet E-F to the d-like bands. If this assignment is correct, the energy separation expected for the two group of bands (3d and s-p-d bands) should amount $\sim 3.0 \text{ eV}$ and the crystal-field splitting of the 4d states $\sim 2.0 \text{ eV}$. Both figures are smaller than the experimental ones but, as already pointed out⁽¹⁾, the energies of these states could easily be in error of several electronvolts. In their SCF-tight binding calculation for SrTiO_3 , Soules et al.⁽⁴⁾ included the excited 4s and 4p orbitals of titanium as well as the contracted 5s and 5p orbitals of strontium but not the 4d orbitals. They find overlapping subbands well separated from the top of the e_g band ($\sim 8 \text{ eV}$) and spread over more than 15 eV. From this result a broadened DOS function is expected, due to the large dispersion of the bands, which might hardly account for the narrow structures E and F.

Similar considerations apply to BaTiO_3 provided the 4d state is replaced with the 5d state of the Ba^{++} ion. To give support to the above model we compare in Fig. 4 the L_{III} edge of barium titanate with the corresponding K edge of Fig. 1. The striking similarity in the lineshape of the main peak suggest that the same final states are involved, being the initial core states delocalized in momentum space. The relative intensities of the group of structures on the high-energy side of the E peak - also present in SrTiO_3 at slightly lower energies - indicate that they correspond to the same final excited states of predominantly p-like symmetry.

Finally the fact that the A-C features of the K absorption edge are not observed at the L edge, lends support to the hypothesis of excitations localized on the Ti atom with small or no projection on the barium states.

A final remark concerns the relative intensities of the transitions. In the X-ray range the photon momentum k_{ph} is comparable to the dimension of the Brillouin zone, and it is no longer correct to think in terms of vertical transitions in the k space. Momentum conservation allows non-vertical interband transitions between points of the Brillouin zone having different symmetries. By considering, for instance, that in perovskites a strong mixture of the d

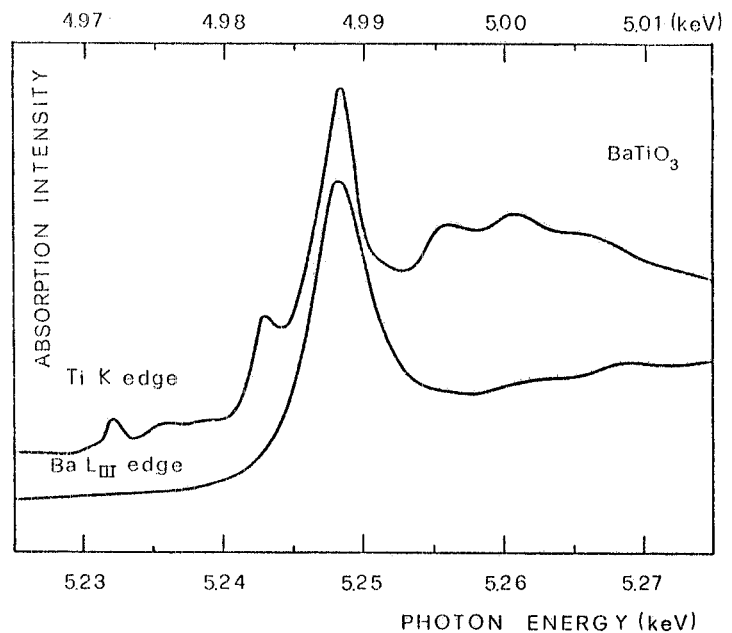


FIG. 4 - Comparison between the K and L_{III} spectra of BaTiO_3 in the tetragonal phase. The lower scale refers to the L_{III} edge of Ba. Peak E of the K edge is made coincident with that of the L_{III} edge in order to stress the similarity among the structures.

wavefunctions of Ti with the oxygen p states occurs at the end of the Brillouin zone (15% and 30% mixing for the t_{2g} and e_g orbitals at the R point for SrTiO_3 respectively⁽⁵⁾), a considerable dipole contribution to the $1s - 3d$ transition is expected in addition to the electric quadrupole term.

To summarize, we have shown that the near edge structures of the transition metal perovskites are reasonably well correlated in a direct way to the conduction band DOS of the crystal, at least for the lowest empty d bands. Many body effects, such as relaxation⁽¹⁹⁾, multiple spitting etc. due to the switching of the core hole, and matrix element effects induce perturbations which apparently do not distort the conduction-band shape appreciably.

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