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Model calculation of core level XPS spectra in early 3d-metal compounds

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Abstract. — Using a configuration-interaction impurity-Anderson model we calculate core-hole X-ray Photoemission Spectra (c-XPS) for some early Transition Metal (TM) insulating compounds. Because in these compounds the valence (ligand) band is completely filled, the TM on-site Coulomb repulsion $U_{66}$ is treated exactly, as well as the 3d-core hole interaction $U_{dc}$. The ground state of such a ligand-TM system with a nominally $d^0$ cation is described as a mixture of purely $d^0$ ionic state, and charge-transfer screened $d^1L$ and $d^2L^2$ states where $L$ denotes a hole in the ligand band. Our simplified model enables us to understand why c-XPS satellites are still present in CaF$_2$ or CaO, like in light TM compounds, but absent for KF compounds. In addition to $U_{66}$ and $U_{dc}$, the other relevant parameters are the ligand-to-metal charge-transfer energy $\Delta$ and the corresponding hybridization $V$ (related to the metal-ligand transfer integrals). Finally quite a good fit to 2p$_{3/2}$-XPS of TiO$_2$ is obtained by using the parameter values estimated from (i) a LMTO band structure calculation of TiO$_2$, and (ii) another calculated fit of the K(Ti) pre-edge absorption spectrum in TiO$_2$.

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1. Introduction.

Transition-metal (TM) compounds have long been of great interest in solid-state physics, even more since the discovery of high-temperature superconductivity in copper oxides. As far as the electronic structure of insulating TM compounds is concerned, band-structure calculations in which exchange and correlation effects are replaced by effective one-electron potentials happen to predict energy gaps, for example, which are an order of magnitude smaller than experimentally observed. In order to obtain information on the correlated nature of the considered 3d-electron systems, the analysis of the core level X-ray photoemission spectra (c-XPS) is certainly one of the most useful tools ([1-3] and Refs. therein). As for the c-XPS in TM compounds, the first successful attempt to give a quantitative interpretation of the spectra was made by van der Laan et al. [4] for copper dihalides, following earlier work by Larsson and Braga [5]. Quite generally it is possible to state that the c-XPS of TM compounds exhibits not only a main line for which the sudden creation of a core hole in the system state is screened as well as possible, but also satellite peaks arising from excitations of the electron system containing the core hole ([4-7] and Refs. therein). In this paper we are interested in the simplest mechanism responsible for the main-line-versus-satellite-structure in the c-XPS of early 3d TM compounds, which have been less studied than the late ones.

Recently and in good agreement with experiment, Bocquet et al. [8] applied a cluster-type configuration interaction model ([4, 5], see also [9, 10]) to perform a systematic analysis of 2p-XPS for late TM (Mn, Fe, Co, Ni, Cu) compounds, specially oxides and sulphides. It seems very tempting to extend the configuration-interaction Anderson-type approach (or a simplified version) to the case of some early TM compounds (Ca, Sc, Ti...), at least to test it numerically (although an additional mechanism has been proposed by de Boer et al. [6] for lighter TM compounds, specially in their vapor-phases [1]). Similarly to the interpretation of the c-XPS satellites in early rare-earth insulating compounds [2, 3, 11, 12], the corresponding satellites in the early TM insulating compounds under consideration are then viewed, similarly to the late TM compounds, as originating from charge transfer between 3d and ligand (anion) orbitals (see Ref. [13] for a systematic discussion of charge transfer and Mott-Hubbard types of TM compounds). Moreover the satellite peaks of an insulating TM compound are often observed more clearly than those of the corresponding TM [14]. Because of differing screening situations, the 3d Coulomb interaction used to interpret the K(Ti) pre-edge absorption in TiO₂ (\(U_{dd} \sim 5\) eV) [9] was found to be much larger than in early TM-metallic systems (\(U_{dd} \sim 1\) - 2 eV). (As an example, \(U_{dd}\) for an isolated V atom in Cu metal was found to be about 1.1 eV [16]). The model calculation of the present paper is based on the filled-band impurity-type configuration-interaction Hamiltonian which can be solved without any approximation because of the filled character of the ligand band (LB) — or valence band — [12]. In this simple model, the physics of the c-XPS is described in terms of a few pertinent parameters, i.e., the on-site Coulomb repulsion \(U_{dd}\), the charge-transfer energy \(\Delta\), which is necessary to transfer one electron from the LB to the metal orbitals, the hybridization energy \(V\) related to the metal-ligand transfer integrals (which mix the previously considered types of states), and the core hole-d electron Coulomb attraction energy \(U_{dc}\).

The paper is organized as follows. In section 2 we recall our model formulation of c-XPS in the case of a series of early TM insulating compounds nominally characterized by a 3d⁰ configuration in the ground state. Then we give some results and general discussion relevant to the early 3d TM-compounds considered as well as K and Ca-compounds (Sect. 3). In section 4 we try to find out the best parameters to fit the experimental results of 2pₓᵧ-XPS in TiO₂ [7, 17, 18] in conjunction with a previous theoretical fit to K(Ti) pre-edge absorption spectra [15] and a previous band structure calculation of TiO₂ [19].
2. Model formulation of c-XPS in some early TM insulating compounds.

We consider early TM insulating compounds characterized by the following band structure ([19] for ex.) : a completely filled LB, mostly arising from the anion states and separated by an energy gap of a few eV from the empty conduction d bands, $t_{2g}$ and $e_g$ which often happen to be separated from each other by another gap. Actually in our simplified formulation we only keep in mind an electron system consisting of a filled LB and a degenerate 3d TM level with the corresponding core level (2s or 2p TM level). Similarly to the case of the 4f$^0$ La insulating compounds (La$_2$O$_3$, LaF$_3$ [20]), the 3d level in the ground state of the TM compound is assumed to be well above the LB, so that it is practically empty; this corresponds to the nominally 3d$^0$ configuration. However, due to configuration interaction, we have to consider a strong mixture of 3d$^0$ and 3d$^1L$ configurations where $L$ means a ligand hole in the LB (also see the appreciable hybridization $V$ found between the LB and the 3d states by Ref. [19]). Actually we also consider 3d$^2L^2$ in the ground state. In the final state of the c-XPS, the 3d level is pulled down by the core hole potential $-U_{dc}$ and a similar configuration interaction mixture takes place between $\zeta$3d$^1L$ and $\zeta$3d$^2L^2$, where $\zeta$ labels the core hole. It is interesting to notice the analogy of the present situation with what happens in copper dihalides [4] or CuO compounds [21], for example, where 3d$^{10}L$ and 3d$^9$ configurations are strongly mixed. The Hamiltonian of our present system is written as :

\[
H = \sum_{k, \nu} \varepsilon_L(k, \nu) \ a_L^+(k, \nu) a_L(k, \nu) + \varepsilon^0_d \sum_{\nu} a_d^+(\nu) a_d(\nu) + \varepsilon_c a_c^+ a_c + \\
+ \frac{V}{\sqrt{N}} \sum_{k, \nu} [a_L^+(k, \nu) a_d(\nu) + \text{h.c.}] + \\
+ U_{dd} \sum_{\nu \neq \nu'} a_d^+(\nu') a_d(\nu') a_d(\nu) a_d(\nu') - (1 - a_c^+ a_c) U_{dc} \sum_{\nu} a_d^+(\nu) a_d(\nu) \tag{2.1}
\]

where $\varepsilon_L(k)$, $\varepsilon^0_d$ and $\varepsilon_c$ are the energies of the LB states, 3d level and core level respectively and $a_L^+(k, \nu)$, $a_d^+(\nu)$ and $a_c^+$ are the electron creation operators in the corresponding states. Here $k$ denotes the index of energy level ($k = 1, \ldots, N$) in the LB and $\nu$ specifies both the spin and orbital degeneracies ($\nu = 1, \ldots, N_d$). Actually $N_d$ can be taken between 2 (only spin degeneracy) and 10 (full d spin-orbital degeneracy). However the spin and orbital degeneracies for the core states are disregarded as well as the corresponding spin-orbit coupling (see [21] for ex.), since in the present simplified model we do not try to describe the full (core-2p) multiplet structure but only one component (2p$^3$ $\pi^2$). Similarly the cubic crystal field effect (see [21] for ex.) on the $\varepsilon^0_d$ level is ignored since it is not a basic parameter to obtain the satellite features. The Hamiltonian used in equation (2.1) is based on a broken translational symmetry for the 3d-states of the TM-ion (3d-single site model). Such an approximation is expected to make sense if the dispersive character of the d-bandwidth is small as it is usually the case in 3d insulating compounds. We could, of course, also break the anion translational symmetry ending up with a much used cluster calculation ([4, 5, 8, 11, 21] and Refs. therein) but the LB width is usually quite large (see [19] for ex.) and therefore not negligible. Equation (2.1) simply treats the 3d-states of the TM-ion as impurity states (the core-hole potential $U_{dc}$ acting like an impurity potential) in a lattice formed by the itinerant ligand states. Let us recall that in the case of the present filled LB, it is easy to derive exact solutions of the preceding « two-electron » Hamiltonian (2.1) [2, 3, 12]. The ground state $|g\rangle$, where the core hole is occupied ($a_c^+ a_c = 1$) is then expressed as a linear combination of the following basis states :
\[ |d^0\rangle = \prod_{k=1}^{N} \prod_{\nu=1}^{N_d} a_d^\dagger (k, \nu) a_c^\dagger |\text{vac}\rangle \]  
\[ |d^1, L (k)\rangle = \frac{1}{\sqrt{N_d}} \sum_{\nu} a_d^\dagger (\nu) a_L (k, \nu) |d^0\rangle \]  
\[ |d^2, L (k_1) L (k_2)\rangle = \]  
\[ \left\{ \begin{array}{c} \sqrt{\frac{2}{N_d(N_d - 1)}} \sum_{\nu_1 > \nu_2} a_d^\dagger (\nu_1) a_L (k_1, \nu_1) a_d^\dagger (\nu_2) a_L (k_1, \nu_2) |d^0\rangle (k_1 = k_2) \\ \sqrt{\frac{1}{N_d(N_d - 1)}} \sum_{\nu_1 > \nu_2} a_d^\dagger (\nu_1) a_L (k_1, \nu_1) a_d^\dagger (\nu_2) a_L (k_2, \nu_2) |d^0\rangle (k_1 \neq k_2) \end{array} \right. \]  

where \(|\text{vac}\rangle\) is the vacuum state. Also each final state \(|f\rangle\) of the c-XPS is expressed, apart from the emitted photoelectron, as a linear combination of the following states:

\[ |d^0, \varepsilon\rangle = a_c |d^0\rangle \]  
\[ |d^1, L (k), \varepsilon\rangle = a_c |d^1, L (k)\rangle \]  
\[ |d^2, L (k_1) L (k_2), \varepsilon\rangle = a_c |d^2, L (k_1) L (k_2)\rangle. \]

An important quantity which characterizes our model system is the ligand-to-metal charge transfer energy \(\Delta\) defined by the energy difference between the 3d\(^0\) and 3d\(^1\)\(L\) configurations as follows:

\[ \Delta \equiv E [3d^1 L] - E [3d^0] = \varepsilon_{L}^0 - \varepsilon_{L}^0, \]  

where \(\varepsilon_{L}^0\) is centre of the LB (hereafter taken as the energy origin). In our model, we treat the filled LB as a finite periodic system consisting of \(N\) discrete levels with equal spacing so that \(\varepsilon_{L}(k)\) of equation (2.1) is:

\[ \varepsilon_{L}(k) = \varepsilon_{L}^0 - W/2 + (W/N) \left( k - 1/2 \right) \quad k = 1, \ldots, N. \]

In the following numerical results, we put \(N = 6\), but this small number is already sufficient to provide a good convergence [12]. Also along the present paper, we take \(W = 5.5\) eV which gives a good order of magnitude of the width of a LB in a typical kind of TM compounds we are considering: actually the precise value of 5.5 eV is taken from a LMTO band structure calculation [19] and concerns the 2p O band of rutile TiO\(_2\). Finally, for simplicity, we put \(N_d = 2\), in the following numerical applications. However, the essential features of the spectrum do not change much with \(N_d\), provided that \(N_d V^2\) is kept constant [12]. That means that e.g. \(V = 6\) eV with \(N_d = 2\) is essentially equivalent to \(V = 3.46\) eV with \(N_d = 6\) (like \(t_{2g}\)) or to \(V = 2.68\) eV with \(N_d = 10\) (like \(t_{2g} + e_g\)).

Disregarding the interaction of the emitted photoelectron with other electrons (sudden approximation), the c-XPS is finally expressed as:

\[ F(E_B) = \sum_{f} |\langle f | g \rangle|^2 (\Gamma/\pi) \left( |E_B + E_g - E_f|^2 + \Gamma^2 \right) \]  

where \(E_B\) is the electronic binding energy obtained by subtracting the kinetic energy \(\varepsilon\) of the photoemitted core electron from the energy \(\omega\) of the incident photon \((E_B = \omega - \varepsilon)\); \(\Gamma\) labels the spectral broadening of our empirical Lorentzian function (2.10) arising from the finite
lifetime of the core hole as well as the experimental resolution width. Unless specified differently, $\Gamma = 1$ eV in the following.

3. General discussion for c-XPS in early 3d insulating compounds.

Let us first remark that in equation (2.1), $U_{dd}$ and $U_{dc}$ are not really independent parameters. In our numerical calculation we take the parameter value $U_{dd}$ somewhat smaller than (or at most equal to) $U_{dc}$ because the average distance between two d electrons is usually larger than the distance between a d- and a core-electron ([6, 8] and Refs. therein). For free atoms, ratios $U_{dd}/U_{dc}$ have been found to vary between 0.7 when $c = 2p$ to 0.9 when $c = 3p$ [6]. In figure 1 we exhibit c-XPS spectra for a range of ratios from $U_{dd}/U_{dc} = 0.666$ (Fig. 1a) to 0.875 (Fig. 1f), which seems to be reasonable. Actually figure 1 summarizes a qualitative study of the effect of increasing the couple $(U_{dd}, U_{dc})$ with respect to $\Delta$ fixed. The last parameter has

![Graphs showing c-XPS spectra for various hybridization strengths](image)

Fig. 1. — c-XPS spectra in 3d$^9$ compounds plotted against binding energy for various hybridization strengths $V = 1, 2, \ldots, 7$ eV and with $(U_{dd}, U_{dc}) = (2, 3)$ eV for (a); $(3, 4)$ eV for (b); $(4, 5)$ eV for (c); $(5, 6)$ eV for (d); $(6, 7)$ eV for (e); $(7, 8)$ eV for (f). The other parameters are $\Delta = 4$ eV; $N_d = 2$; $\Gamma = 1$ eV.
been chosen to be 4 eV with a LB width of 5.5 eV, i.e. a band gap of 1.25 eV between $\varepsilon_d^0$ and the highest state of LB, before considering any effect of $U_{dd}$ or $U_{dc}$ on $\varepsilon_d^0$. From figure 1 and quite generally it is possible to distinguish two regimes of parameter values [13, 8] : (1) $(U_{dd}, U_{dc}) \ll \Delta$ like in figure 1a where the satellite is practically absent from the spectra ; (2) $(U_{dd}, U_{dc}) \geq \Delta$ like in figures 1c, ..., 1f, where the satellite is clearly visible, even for small $V$. For a simplified analytical model restricted to two configurations we refer to reference [4] : this model relates the position of the satellite and its intensity to $\Delta$, $V$ and $U_{dd}$ (but does not include $U_{dc}$).

Veal and Paulikas [7] reported 2p-XPS for 2+, 3+ and 4+ cations of CaF$_2$, ScF$_3$ and TiF$_4$ fluorides (see their Fig. 7). For all these early 3d insulating compounds where cationic configuration is nominally pure 3d$^0$4s$^0$, satellites are about 10 to 15 eV separated from the main core line. The situation would be similar for CaO, Sc$_2$O$_3$ and TiO$_2$ [6, 7] (see next section for TiO$_2$). Satellites simply replicate the main spin-orbit doublet without overlapping it. Unfortunately for V$_2$O$_5$ the satellite structure (especially $V(2p_{3/2})$) is not easily observed because of the superposition of a sharp O 1s peak at about the same energy range [22]. For the calcium compounds (CaF$_2$, CaO), the satellite peaks are the weakest but still visible. However in K 2p XPS of potassium halides like KF (Fig. 11 of Ref. [7]), where the cationic configuration also corresponds to 3d$^0$4s$^0$, no satellite structure can be discerned and attributed to local screening states. In this case the unfilled 3d states are located too far above the LB (wide-band-gap material) so that, even in the final state of the 2p-XPS, the 3d levels are still well above the LB and cannot participate to the local screening of the core hole. In our model calculation (Fig. 2) we show that, if the transfer energy $\Delta$ becomes larger and

$$\Delta (\text{eV}) = 9$$

![Diagram](image_url)

Fig. 2. — c-XPS spectra in 3d$^0$ compounds plotted against binding energy for various charge-transfer energy $\Delta = 3, 4, \ldots, 9$ eV and with $(U_{dd}, U_{dc}) = (3, 4)$ eV ; $(V, N_d) = (5 \text{ eV}, 2) ; \Gamma = 1 \text{ eV}$. 
larger, from 3 to 9 eV, then the satellite becomes smaller and smaller (case of Ca-compounds) and finally disappears (case of K-monohalides) for \( \Delta \ll (U_{dd}, U_{dc}) \). It is interesting to underline that, on the opposite of \( K^+ \), the \( \text{Ca}^{2+} \) cation in the final state of the c-XPS, shows low-lying 3d behavior which is typical of the cation considered in the whole TM-series of insulating compounds. The important common feature is that, in the final state, the first unoccupied still accessible level is 3d. The low-binding-energy c-XPS peak roughly corresponds to a locally well screened state 3d\(^1\) and the higher binding energy satellite to a locally poorly screened state 3d\(^0\). The fact that K and Ca ions show different but predictable satellite structures provides evidence in support of the 3d screening model of the core hole. Also the energy separation between the main and satellite peaks (see Eq. (10) of Ref. [4]) is observed to increase in the series \( \text{CaF}_2, \text{ScF}_3, \text{TiF}_4 \) [7] or \( \text{CaO}, \text{Sc}_2\text{O}_3, \text{TiO}_2 \) [6]: this would be in agreement with an increase of hybridization \( V \) in our model from Ca to Ti compounds (Fig. 1d, e or f).

4. Case of 2p-XPS in (rutile) \( \text{TiO}_2 \).

There has been a large number of experimental studies on 2s or 2p Ti c-XPS in \( \text{TiO}_2 \) compounds (for ex. [7, 17, 18]) as well as in related insulating oxides like \( \text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4 \) [23] showing satellites on the high-binding energy side as generally discussed in the preceding section. In reference [23], however, the authors did not clearly notice and interpret the characteristic satellites. Furthermore, as far as we know, there has been no theoretical attempt to interpret and to fit the c-XPS of \( \text{TiO}_2 \) quantitatively, if we exclude very

Fig. 3. — c-XPS spectra in 3d\(^0\) compounds plotted against binding energy for various 3d-core hole interaction \( U_{dc} = 5, \ldots, 8 \) eV and with \( U_{dd} = 5 \) eV; \( (V, N_d) = (6 \text{ eV}, 2) \); \( \Delta = 4 \) eV; \( \Gamma = 1 \) eV.
preliminary results [19] within the present model where the calculated satellite peak happened to be too small. Recently the K(Ti)-pre-edge absorption of TiO$_2$ [15] has been successfully interpreted using a somewhat similar Hamiltonian as equation (2.1) with, in particular, the following parameter values: $\Delta = 4$ eV, $U_{dd} = 5$ eV and $U_{dc} = 6$ eV. It is interesting to perform a c-XPS calculation (Fig. 3) of TiO$_2$ using the same $\Delta$ and $U_{dd}$ parameter values as for K(Ti)-pre-edge, allowing $U_{dc}$ to vary from 5 eV ($U_{dd}/U_{dc} = 1$) to 8 eV ($U_{dd}/U_{dc} = 0.625$). Also the width of the LB (see Sect. 2) has been taken from an LMTO band structure calculation of TiO$_2$ in the rutile phase [19] and $V$ has been fixed at 6 eV with $N_d = 2$ (or equivalently $V = 3.46$ eV with $N_d = 6$) in order to obtain a satellite at about 13.6 from the main line [7, 17, 18]. From figure 3 we see that the increase of strength of $U_{dc}$ has a direct effect on the increase of intensity of the satellite. Next we just test the influence of $\Gamma$ (appearing in Eq. (2.10)) on the c-XPS (Fig. 4) (see Ref. [8] for a similar range of values of $\Gamma$). Quite obviously $\Gamma$ does not change the spectra, but to smaller $\Gamma$'s correspond of course more peaky spectra. Finally we report (Fig. 5) the experimental 2p-XPS of TiO$_2$ after background subtraction measured by reference [17], as well as our calculated fit with $\Delta = 4$ eV, $V = 6$ eV, $U_{dd} = 5$ eV, $U_{dc} = 7$ eV and $\Gamma = 0.7$ eV. Also for this set of parameters, table I exhibits the weights $w(3d^i)$ of the various 3d$^i$ configuration contributions with $i = 0, 1, 2$. Due to strong hybridization $V$, the ground state is, as expected, a fairly strong mixture of $|d^0\rangle$ ($\sim 46\%$) and $|d^1L\rangle$ ($\sim 46\%$). In the final state, $|f_{main}\rangle$, corresponding to the most intense photoemission line, is also a strong mixture of $|cd^1L\rangle$ (55.0 $\%$), $|cd^2L^2\rangle$ (27.1 $\%$) but also $|cd^0\rangle$ (17.9 $\%$) whereas $|f_{sat}\rangle$, corresponding to the satellite peak, is due to $|cd^2L^2\rangle$ (57.1 $\%$), $|cd^0\rangle$ (38.1 $\%$) and $|cd^1L\rangle$ (4.8 $\%$). Because of

![Diagram](image_url)

**Fig. 4.** — c-XPS spectra in 3d$^0$ compounds plotted against binding energy for various spectral broadenings $\Gamma = 0.7, 0.8, 1.3$ and with $(U_{dd}, U_{dc}) = (5, 7)$ eV; $(V, N_d) = (6$ eV, 2); $\Delta = 4$ eV.
CALCULATION OF CORE-XPS SPECTRA IN 3d-METAL COMPOUNDS

Fig. 5. — Dotted line: experimental 2p-XPS of TiO$_2$ after background subtraction (see Ref. [11]). Full line: calculated 2p$_{3/2}$-XPS of TiO$_2$ with the following parameters: $(U_{dd}, U_{dc}) = (5, 7)$ eV; $(V, N_d) = (6$ eV, 2); $\Delta = 4$ eV and $\Gamma = 0.7$ eV.

Table I. — Weights $w$ of 3d$^0$, 3d$^1$ and 3d$^2$ components [13], averaged 3d electron number $\langle n_d \rangle$, in the eigenstates $|g\rangle$, $|f_{\text{main}}\rangle$ and $|f_{\text{sat}}\rangle$; $E_B$ and $A$ are the position and amplitude of $|f_{\text{main}}\rangle$ and $|f_{\text{sat}}\rangle$; the corresponding energy separation between satellite and main line is here $\sim 13.6$ eV. The parameter values are the following: $(U_{dd}, U_{dc}) = (5, 7)$ eV; $(V, N_d) = (6$ eV, 2); $\Delta = 4$ eV and $\Gamma = 0.7$ eV.

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<th>$w$(3d$^1$)</th>
<th>$w$(3d$^2$)</th>
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</table>

the core hole effect the contribution of the 3d$^2$ configuration happens to be quite significant in the final state (it is only 7.8% in the ground state). It would even be interesting to extend the present model to test if the 3d$^3$ contribution is negligibly small.

Finally let us give the following comment on the value of $\Delta$. According to the Hartree-Fock approximation of equation (2.1) in the initial state, $\Delta$ should be replaced by $\Delta_{\text{eff}} = \Delta + \langle n_d \rangle U_{dd}$, which takes the electronic correlations into account, at least in a mean field approximation, and gives about 7.1 eV (with $\langle n_d \rangle \sim 0.62$). This value of $\Delta_{\text{eff}}$, i.e. $\varepsilon_{2g}$ counted from the centre of the LB, is in rough agreement with the actual position of the $t_{2g}$ band in reference [19].

5. Conclusion.

In this paper we essentially calculated c-XPS resulting from the creation of a core hole c within the filled band impurity Anderson model. Our simplified calculations seem to explain well the spectra of a series of early TM insulating compounds, characterized by a nominally
3d$^0$ configuration in the ground state, including those compounds which involve a pre-transitional element such as K or Ca. Moreover, without including any additional mechanism [6], our model is able to fit reasonably well the 2p$_{3/2}$-XPS of TiO$_2$ using values of parameters in accord with a previous band structure calculation [19] and with a recent calculated K(Ti) pre-edge absorption spectrum [15]. From the value of $\Delta$, $U_{dd}$ and $U_{de}$ we conclude that TiO$_2$ resembles the late TM compounds as far as the interpretation of the c-XPS spectra is concerned: TiO$_2$ belongs to the charge transfer regime [13, 8], i.e. $\Delta \leq (U_{dd}, U_{de})$. Probably Sc and Ca insulating compounds are at the border line of this regime.

The present model calculation is restricted to nominally pure 3d$^0$ configuration in the ground state like Ti$^{4+}$ insulators. A very interesting extension would be to consider for example a nominally 3d$^{0.5}$ metallic system, like Li$_2$Ti$_2$O$_4$, and to treat it as a mixed valence system (Ti$^{3+}$, Ti$^{4+}$) in the ground state, which remains out of the scope of a single Ti site model. One way to improve the present formulation, by including multi Ti site interactions, would then be to extend equation (2.1) to a periodic Anderson model [3], i.e. the two (hybridized) band Hubbard Hamiltonian. This would be adequate to describe the evolution of c-XPS during the insulating-metallic transition when going from Li$_{4/3}$Ti$_{5/3}$O$_4$ to LiTi$_2$O$_4$ or TiO$_2$ to Ti$_2$O$_3$ or also V$_2$O$_5$ to VO$_2$. This study is now in progress.

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