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Electronic structure and core level photoemission spectra in TiO₂ compounds

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Abstract. In this paper we first calculate a standard ‘linear muffin-tin orbital’ band structure (including combined correction and exchange correlation) for TiO₂ compounds in rutile structure. The outgoing bands, especially the last valence (mostly O 2p states) and first conduction (mostly Ti t_{2g} states) bands, are fairly hybridized. We then use the information contained in the previously considered density of states to build a simplified electronic structure of TiO₂ in order to interpret the Ti core-level photoemission spectra in the simplest way. To achieve this we use the filled band impurity Anderson model which treats the Ti 3d electron–electron correlations and we incorporate the 3d-core hole interaction. Although our model is quite crude from the point of view of the one-electron band structure calculation, it contains many-electron features which can be solved exactly and which are sufficient to roughly describe the satellite structure observed in the core photoemission spectra of TiO₂ (as well as related insulating compounds like Li_{4/3}Ti_{5/3}O₄ or TiF₄, for example).

1. Introduction

There has been quite a large number of experimental studies on 2s or 2p Ti-core-x-ray photoelectron spectra (C-XPS) in TiO₂ compounds (see, for example, Sen *et al* 1976, Veal and Paulikas 1985, Carley *et al* 1987) as well as in related materials like insulating Li_{4/3}Ti_{5/3}O₄ or metallic LiTi₂O₄ compounds (Edwards *et al* 1984). This last spinel material which is a middle high-*T_c* oxide was recently studied in detail by Heintz *et al* (1989) and Durmeyer *et al* (1990). In this paper we will essentially focus our attention, as a first step, on TiO₂ compounds: for instance, if we examine the 2p-XPS spectra of TiO₂, the experimental data show satellites on the high-binding energy side which simply replicate the main spin-orbit doublet without overlapping it: a similar feature appears in TiF₄ (Veal and Paulikas 1985) and LiTi₂O₄ (Edwards *et al* 1984) although in this last case the authors did not clearly notice and interpret the characteristic satellites. Nevertheless, there is a wide consensus to associate the considered satellites to the creation of a core hole during the C-XPS process. Yet, as far as we know, there has been no theoretical attempt to interpret the spectra in a somewhat quantitative way. It is one of the purposes of the present paper to exhibit the first (preliminary) calculation on C-XPS in TiO₂ type compounds, using the filled band impurity Anderson model (Kotani and Parlebas 1985, Kotani *et al* 1988). Another purpose of the present work is to calculate a standard

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'linear muffin-tin orbital' (LMTO) band structure for TiO_2 compounds in rutile structure including 'combined correction' and 'exchange correlation' (Andersen 1975, Skriver 1984); as a matter of fact, this last calculation also provides some information required in the previously considered Anderson model.

The paper is organized as follows. In section 2 we present the TiO_2 LMTO band structure and exhibit the resulting energy dispersion spectrum as well as the various densities of states (DOS). Then in section 3 we keep only the last valence band (essentially O 2p states) and one 3d level which we strongly hybridize within the filled band impurity Anderson model, taking into account an additional important 3d-core hole interaction in order to describe the C-XPS process. Finally, in section 4, we discuss the C-XPS spectra obtained in the considered model in terms of the significant parameters. The conclusion, section 5, is concerned with a few general remarks on related problems.

2. LMTO band structure of TiO_2 and density of states

TiO_2 (rutile) crystallizes in a tetragonal structure with $a = 4.49 \text{ \AA}$, $c = 2.89 \text{ \AA}$ and $u = 0.31$ (Wyckoff 1981). A unit cell contains two Ti atoms and four O atoms. The core charge distribution for Ti and O was obtained through a self-consistent Dirac atomic potential. Electrons up to and including O 1s and Ti 3p were treated as frozen-core electrons. We used two energy panels for the band structure calculation within a local density approximation using the self-consistent LMTO method (Andersen 1975, Skriver 1984) in an atomic-sphere approximation (ASA) where the combined correction is properly included. The scalar-relativistic Schrödinger equation with von Barth-Hedin (1972) exchange correlation was solved. We consider the muffin-tin orbitals of angular momentum s, p and d for O and Ti atoms, thus the matrix to be diagonalized is of order 54×54 . The eigenvalues and eigenvectors were calculated on a grid of 75 k -points in the irreducible 1/16th Brillouin zone.

The calculated energy bands are shown in figure 1. These energy bands are given in the high symmetry directions (Slater 1965) Γ -M-X- Γ -Z-R-X-M-A-Z. We have traced these levels from -0.8 to 1.2 Ryd. The horizontal line EF indicates the bottom of the conduction band (CB). The valence band (VB) extends from -0.72 to -0.1625 Ryd. Another VB lies at about 16.3 eV below the VB maximum (i.e. -0.1625 Ryd) with a width of about 2.6 eV. This lower VB is about 90% of O 2s origin. This band is not presented in figure 1 nor in the density of states curves. We shall not talk of it anymore, and by VB we shall mean the band lying between -0.72 and -0.1625 Ryd which has its maximum at Γ . After a forbidden gap ($E_g \approx 3.06$ eV), the first CB starts with a minimum at a point near R symmetry following the R-X direction. Thus our band scheme shows that TiO_2 is a semiconductor with an indirect forbidden gap of 3.06 eV. In a previous calculation Kazowski and Tait (1979) also obtained an indirect forbidden gap but the CB minimum was found to be at M. They also used LMTO method as we have done here, but performed their calculation (i) without combined correction, (ii) with a small number of basis functions, and (iii) without exchange correlation.

In figures 2(a), (b) and (c), we show the total DOS per unit cell, 2(a), and also the local DOS of s, p and d symmetries in Ti, 2(b), and O, 2(c), Wigner-Seitz spheres (wss). In Ti wss the d symmetry is so dominant that the presence of s and p symmetries is almost unobserved. Thus, in figure 2(d) we show s and p partial DOS in Ti wss. The number of states of different symmetries and of different chemical origins in the VB and CB are tabulated in table 1. From the DOS curves and table 1 we notice that indeed all bands are

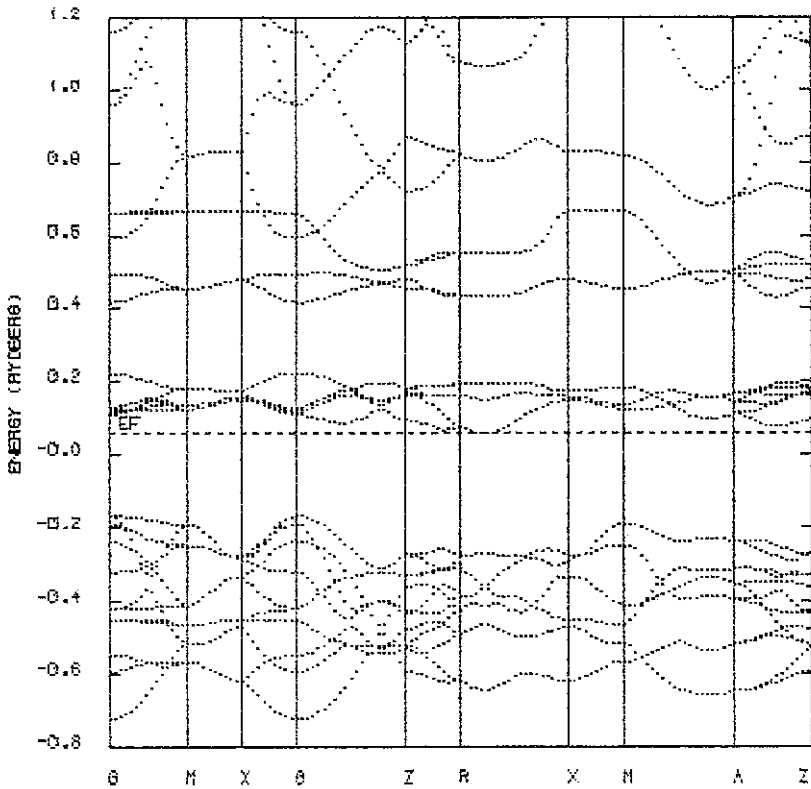


Figure 1. Energy dispersion curves along the Brillouin zone high symmetry directions Γ -M-X- Γ -Z-R-X-M-A-Z. The Γ point has been labelled by the letter Θ .

mixed states, and in each case all different symmetries are present. The VB is mainly of O 2p origin ($\sim 80\%$) but at the same time it also contains 13% Ti d and 7% other symmetries. The first CB is $\sim 75\%$ Ti d (t_{2g}) about 11% each of O p and O d but at the same time it also contains a small amount of Ti p. The presence of Ti p symmetry in this band is more evident from figure 2(d). The Ti t_{2g} band is about 2.3 eV wide. After a forbidden gap of about 2.7 eV from this band we obtain the next conduction band of mainly Ti e_g origin. This band, in turn, is split into two because of the crystal structure. The lower band (about 1 eV wide) is mainly of x^2-y^2 symmetry of Ti origin.

3. Formulation of the c-xps spectra

In order to mimic the preceding band structure of TiO_2 , especially its total DOS, we simply consider a system consisting of a (non-degenerate) discrete VB, which essentially represents a finite number of N 2p states of oxygen, and one 3d level of total (spin + orbital) degeneracy $N_d = 2$ (instead of the t_{2g} band) at the Ti photoexcited site. Then, within the (filled band) impurity Anderson model, the Hamiltonian describing

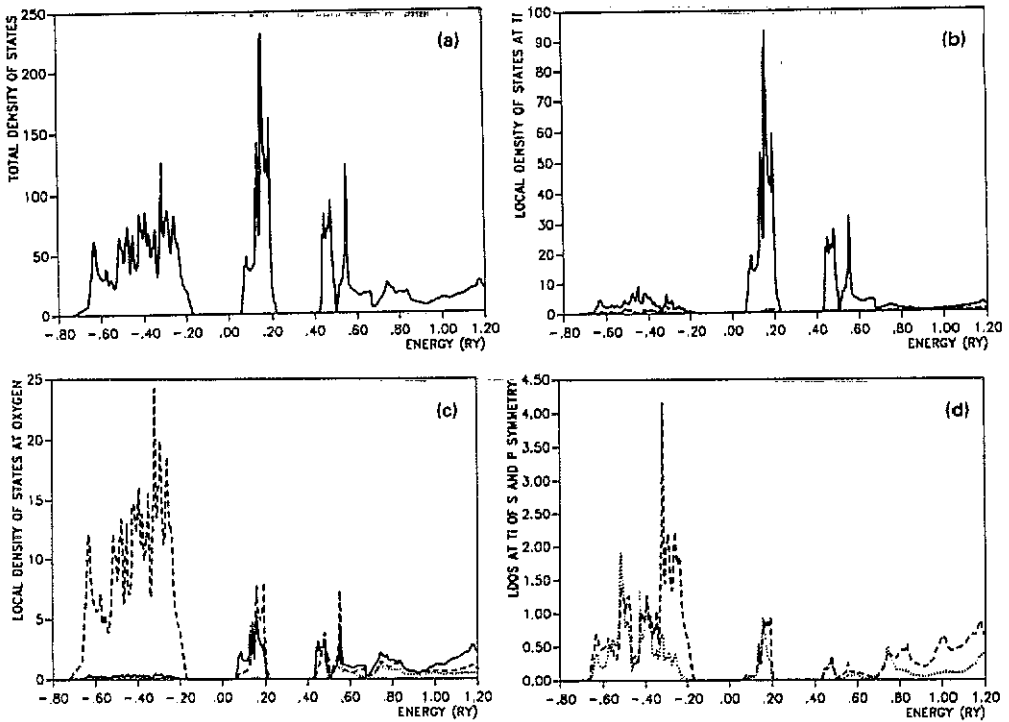


Figure 2. (a) Total DOS per unit cell in TiO_2 compounds; (b) corresponding local DOS of $s(\cdots\cdots)$, $p(\text{---})$ and $d(\text{---})$ symmetries in the Ti Wigner-Seitz sphere; (c) corresponding local DOS of $s(\cdots\cdots)$, $p(\text{---})$ and $d(\text{---})$ symmetries in the O Wigner-Seitz sphere; (d) magnified view of (b) for $s(\cdots\cdots)$ and $p(\text{---})$ symmetries at Ti.

Table 1. Number of states n_m^α of m symmetry in α Wigner-Seitz sphere for the valence and conduction bands of, respectively, O $2p$ and Ti T_{2g} origin (degeneracy $N_d = 6$).

n_m^α	Valence band O $2p$	Conduction band Ti t_{2g}
n_s^0	0.01360	0.00585
n_p^0	4.73642	0.37152
n_d^0	0.10360	0.33100
$n^0 = n_s^0 + n_p^0 + n_d^0$	4.85362	0.70837
n_s^{Ti}	0.22690	0.03300
n_p^{Ti}	0.45410	0.04900
n_d^{Ti}	1.61210	4.50125
$n^{\text{Ti}} = n_p^{\text{Ti}} + n_d^{\text{Ti}}$	2.29310	4.58325
Total in the unit cell		
$n = 2n^{\text{Ti}} + 4n^0$	24	12

the initial state of the C-XPS process is given by Kotani and Parlebas (1985), Kotani *et al* (1988):

$$\begin{aligned}
 H_0 = & \sum_{k\sigma} \epsilon_k a_{k\sigma}^\dagger a_{k\sigma} + \epsilon_{d\sigma} \sum_{\sigma} a_{d\sigma}^\dagger a_{d\sigma} + N^{-1/2} \sum_{k\sigma} (V_{kd} a_{k\sigma}^\dagger a_{d\sigma} + \text{cc}) \\
 & + U_{dd} a_{d\uparrow}^\dagger a_{d\uparrow} a_{d\downarrow}^\dagger a_{d\downarrow}
 \end{aligned} \quad (1)$$

while the Hamiltonian in the final state is written as:

$$H = H_0 - U_{dc} \sum_{\sigma} a_{d\sigma}^{\dagger} a_{d\sigma}. \quad (2)$$

Here ϵ_k and ϵ_{do} are the energies of the VB states and 3d level respectively, and $a_{k\sigma}^{\dagger}$ and $a_{d\sigma}^{\dagger}$ are electron creation operators in these states. Interaction terms V_{kd} , U_{dd} and $-U_{dc}$ ($U_{dc} > 0$), respectively, represent the important hybridization between VB states and the 3d level, the intraatomic Coulomb repulsion between 3d electrons and the strong attractive core hole potential acting on the 3d level to lower it down in the final state. In the case of the present filled band impurity Anderson model let us recall that it is possible to derive exact solutions of the preceding many-electron Hamiltonians H_0 and H . We refer to Kotani and Parlebas (1985) and Kotani *et al* (1988) for details. Let $|g\rangle$ be the ground state of H_0 with energy E_g and the $\{|f\rangle\}$ s all the final states of H with the energies E_f . Here we just recall that a given final state $|f\rangle$ is expressed in the form of double-hole system state like:

$$|f\rangle = \sum_{n_1 n_2} B_{n_1 n_2}^f b_{n_1 \uparrow} b_{n_2 \downarrow} |\Psi\rangle \quad (3)$$

with:

$$|\Psi\rangle = \prod_{k\sigma} a_{d\sigma}^{\dagger} a_{k\sigma}^{\dagger} |\text{vac}\rangle \quad (4)$$

and

$$b_{n\sigma} = \alpha_{nd} a_{d\sigma} + \sum_k \alpha_{nk} a_{k\sigma}. \quad (5)$$

For the values of the coefficients α_{nd} , α_{nk} and $B_{n_1 n_2}^f$, see equations (24), (25) and (30) of Kotani *et al* (1988). Disregarding the interaction of the escaping photoelectron with other electrons we can write the C-XPS spectrum as:

$$F(E_B) = \sum_f |\langle f|g\rangle|^2 (\Gamma/\pi) / [(E_B + E_g - E_f)^2 + \Gamma^2] \quad (6)$$

where E_B is the electronic binding energy obtained by subtracting the kinetic energy ϵ of the photoemitted core electron from the energy ω of the incident photon ($E_B = \omega - \epsilon$); Γ labels the spectral broadening arising from the finite lifetime of the core hole as well as the experimental resolution width. In the following numerical analysis we take $\Gamma = 1$ eV. Also, in order to mimic the preceding total DOS of TiO₂ we put $W = 5.5$ eV for the width of the VB. In our calculations, as already stated, we treat the filled VB as a finite system consisting of N discrete levels with equal spacing:

$$\epsilon_k = \epsilon_{po} - W/2 + (W/N)(k - \frac{1}{2}) \quad k = 1, \dots, N \quad (7)$$

where ϵ_{po} is the centre of the VB, hereafter taken as the energy origin. In the following calculations we put $N = 6$ but this small number, somewhat related to a periodic O₆ cluster (+ one Ti-3d-like orbital) is already sufficient to provide a good convergence (Kotani *et al* 1988). Finally from the total DOS of TiO₂ (figure 2(a)), we choose $\epsilon_{do} - \epsilon_{po} = 7.9$ eV which means that in this insulating compound model the 3d level is put far above the VB in a manner similar to that of the d bands of the LMTO calculation, ϵ_{do} corresponding to the average energy values of Ti t_{2g} and e_g states.

Before discussing the core XPS spectra in the next section let us just recall that the weights of $3d^0$, $3d^1$ and $3d^2$ components in the ground state $|g\rangle$ and in each discrete final state $|f\rangle$ (equation (3)) are easily calculated. For instance, considering a state $|f\rangle$ we have:

$$w(3d^0) = \left(\sum_{n_1 n_2} B_{n_1 n_2}^f \alpha_{n_1 d} \alpha_{n_2 d} \right)^2 \quad (8)$$

$$w(3d^1) = 2 \sum_k \left(\sum_{n_1 n_2} B_{n_1 n_2}^f \alpha_{n_1 d} \alpha_{n_2 k} \right)^2 \quad (9)$$

$$w(3d^2) = \sum_{k_1 k_2} \left(\sum_{n_1 n_2} B_{n_1 n_2}^f \alpha_{n_1 k_1} \alpha_{n_2 k_2} \right)^2 \quad (10)$$

and we can write the averaged 3d electron number contained in this final eigenstate $|f\rangle$ as:

$$\langle n_d \rangle = w(3d^1) + 2w(3d^2). \quad (11)$$

4. Discussion

Our results are shown in figure 3 which exhibits the C-XPS intensity given by equation (6) against the electronic binding energy for various hybridization strengths $V_{kd} \equiv V = 1, 2, \dots, 7$ eV. In the case we consider, since the 3d level is far above the VB in the initial state of C-XPS, the first idea is to represent it by an almost pure Ti^{4+} or d^0 configuration (the spin singlet ground state $|g\rangle$), whereas in the final state when ϵ_{do} has been lowered down to, $\epsilon_d = \epsilon_{do} - U_{dc}$, we mostly expect d^0 and d^1 contributions to the spectrum. In fact as we will explain below, the precise situation is still fairly sensitive to the strengths of the interactions V , U_{dc} and U_{dd} . Actually, in figure 3 and to begin with, the ratio U_{dc}/U_{dd} was arbitrarily taken to be 1.2 but we will discuss this choice later on. Let us first comment on the effect of U_{dc} . From figure 3(a) we note that the strength of the core hole potential $U_{dc} = 2.4$ eV is too small to exhibit any apparent satellite structure. With $U_{dc} = 3.6$ eV, the satellite begins to be visible (figure 3(b)) and with $U_{dc} = 4.8$ eV it is clearly visible (although tiny compared with the main line) at energy positions which increase with increasing V . In order to obtain a satellite at about 13 eV (see table 1 of Veal and Paulikas 1985) it is necessary to take V as high as about 6 eV with $N_d = 2$. This value of the hybridization actually corresponds to $V \approx 3.5$ eV with $N_d = 6$ (like t_{2g}) since it is well known that the essential features of the spectrum do not change much with N_d , provided that $N_d V^2$ is kept constant (Kotani *et al* 1988). In table 2 we see that the ground state corresponding to $V = 6$ eV, $U_{dc} = 4.8$ eV and $U_{dd} = 4$ eV is already a fairly strong mixture of $3d^0$ (~61%) and $3d^1$ (35%). Let us now consider the final states. For the final state $|f_{main}\rangle$ corresponding to the most intense photoemission line at $E_B = -2.64$ eV we obtain again a strong admixture of $3d^0$ and $3d^1$ contributions (respectively 41.3% and 48.4%) with a smaller addition of $3d^2$ weight (10.3%), whereas at $E_B = 11.38$ eV, the satellite position $|f_{sat}\rangle$ is built from $3d^0$ (41.6%), $3d^1$ (21.2%) and $3d^2$ (37.2%) contributions. Hence the satellite photoemission peak originates from the strong mixing between the three configurations in the final state.

Finally we plot (figure 4) the C-XPS spectra for $U_{dc} = 4.8$ eV and $U_{dd} = 2$ eV (again for various hybridization strengths V between 1 and 7 eV) in order to test the influence of the Coulomb repulsion U_{dd} . Apparently there is not much influence since figure 4 resembles figure 3(c). However, if we look at the detailed numbers (see table 3, again

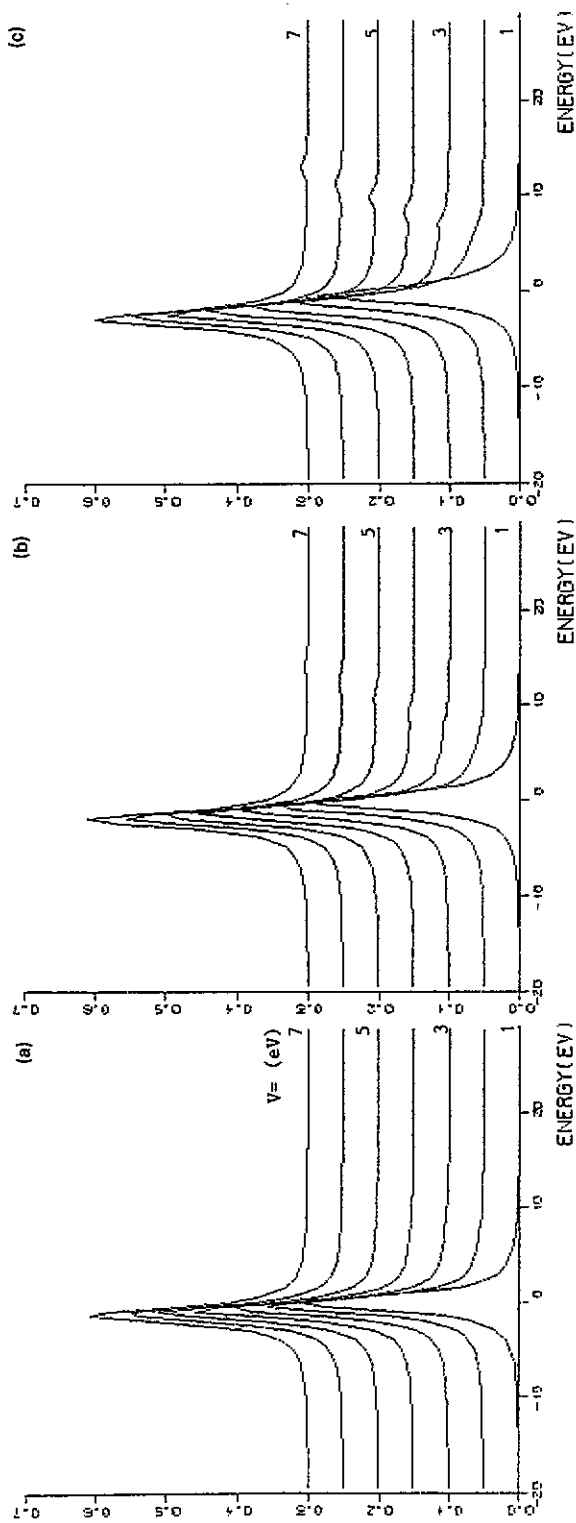


Figure 3. e-XPS spectra in TiO_2 compounds plotted against electronic binding energy for various hybridization strengths V ranging from 1 to 7 eV and for (a) $U_{dc} = 2.4$ eV; (b) 3.6 eV; and (c) 4.8 eV with $U_{dc}/U_{dd} = 1.2$.

Table 2. Weights w of $3d^0$, $3d^1$ and $3d^2$ components and averaged $3d$ electron number $\langle n_d \rangle$ in the eigenstates $|g\rangle$, $|f_{\text{main}}\rangle$ (at $E_B = -2.64$ eV) and $|f_{\text{sat}}\rangle$ (at $E_B = 11.38$ eV) with $U_{\text{dd}} = 4.0$ eV, $U_{\text{dc}} = 4.8$ eV and $V = 6$ eV (degeneracy $N_d = 2$). The corresponding energy separation between satellite and main line is here 14.02 eV.

	$w(3d^0)$	$w(3d^1)$	$w(3d^2)$	$\langle n_d \rangle$
$ g\rangle$	0.609	0.352	0.039	0.429
$ f_{\text{main}}\rangle$	0.413	0.484	0.103	0.690
$ f_{\text{sat}}\rangle$	0.416	0.212	0.372	0.956

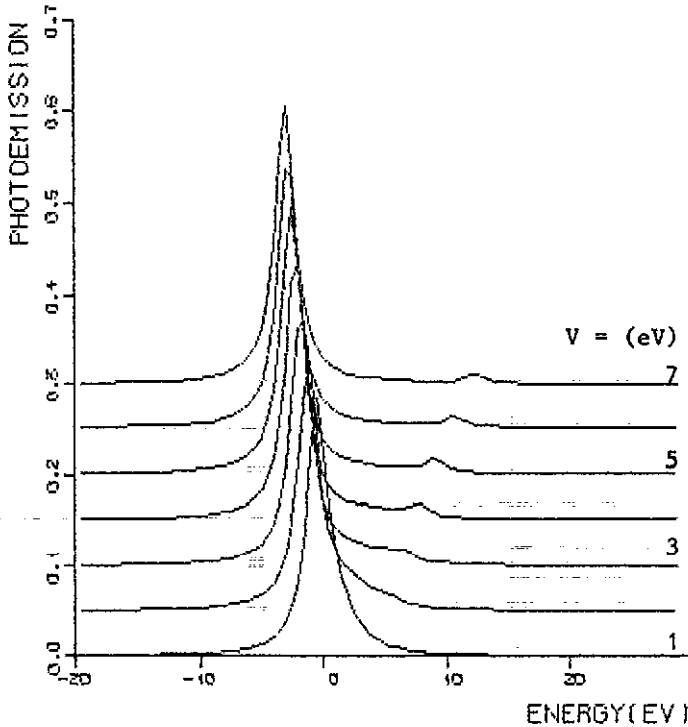


Figure 4. c-XPS spectra in TiO_2 compounds plotted against electronic binding energy for various hybridization strengths V ranging from 1 to 7 eV and for $U_{\text{dc}} = 4.8$ eV with $U_{\text{dc}}/U_{\text{dd}} = 2.4$ (i.e. $U_{\text{dd}} = 2$ eV).

Table 3. Weights w of $3d^0$, $3d^1$ and $3d^2$ components and averaged $3d$ electron number $\langle n_d \rangle$ in the eigenstates $|g\rangle$, $|f_{\text{main}}\rangle$ (at $E_B = -4.13$ eV) and $|f_{\text{sat}}\rangle$ (at $E_B = 8.87$ eV) with $U_{\text{dd}} = 2.0$ eV, $U_{\text{dc}} = 4.8$ eV and $V = 6$ eV (degeneracy $N_d = 2$). The corresponding energy separation between satellite and main line is here 13.00 eV.

	$w(3d^0)$	$w(3d^1)$	$w(3d^2)$	$\langle n_d \rangle$
$ g\rangle$	0.428	0.465	0.107	0.679
$ f_{\text{main}}\rangle$	0.212	0.520	0.268	1.056
$ f_{\text{sat}}\rangle$	0.045	0.007	0.948	1.903

given for $V = 6$ eV) we understand that U_{dd} is an essential parameter, even in this unfavourable case. First, of all, with $U_{dd} = 2$ eV, more than 10% of $3d^2$ configuration is already allowed in the ground state $|g\rangle$ of table 3, whereas less than 4% was allowed in table 2. We can then say that the essential contribution (almost 95%) to the satellite peak in table 3 comes from the $3d^2$ configuration when U_{dd} is lowered from 4 eV to 2 eV, i.e. with less coulombic repulsion. As a final remark we would like to point out that $U_{dd} = 2$ eV for Ti seems to be a more reasonable value than 4 eV for a transition element at the beginning of the series. However, the experimental value of 13.3 eV given by Veal and Paulikas (1985) for the energy separation between the satellite and the main line lies in between the values corresponding to table 2 (figure 3(c): 14.02 eV) and to table 3 (figure 4: 13.00 eV) for $V = 6$ eV.

5. Conclusion

In this paper we presented LMTO band structure results of TiO_2 compounds and then replaced the actual VB with a simplified discrete rectangular shaped band in order to calculate a many-electron C-XPS spectra within the filled band impurity Anderson model. Our results seem to be reasonable both in the parameter values and the spectral features. One possible improvement of the present work would be to incorporate the LMTO VB into the Anderson model. However, another big approximation inherent of the impurity model was to replace the t_{2g} sub-band by a single d level at the irradiated Ti site. The only way to improve this situation would be to extend the present theory to a periodic Anderson model (Parlebas *et al* 1991, and references therein) where there would actually be two hybridized bands. This would be adequate to describe the evolution of the C-XPS spectra during the insulating-metallic transition when going from $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ to LiTi_2O_4 which is a mixed valence metal with both Ti^{3+} and Ti^{4+} configurations and then to MgTi_2O_4 which is essentially a Ti^{3+} metal. Such work is now under investigation.

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