

# Theoretical Interpretation of the Valence X-Ray Photoelectron Spectrum of TiC

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The valence X-ray photoelectron spectrum of TiC is interpreted in terms of the density of states and in terms of a simple model for transition matrix elements. The conceptual difficulties arising with both the initial and the final state are discussed.

**Key words:** TiC, X-ray photoelectron spectrum of ~

## 1. Introduction

Results of energy band structure calculations have been used successfully to interpret the relative intensities of soft X-ray emission spectra [1, 2]. However, there is little experience available about the interpretation of relative intensities for photoelectron spectra in similar terms. Usually these intensities are correlated with the density of states of the bulk [3, 4]. Even in a simple one-electron approach severe conceptual difficulties arise. Suppose that within the premises of Koopmans' theorem the initial state for a calculation of photoionization cross-sections is given by an eigenfunction  $\langle z | i \rangle$  of a crystal one-electron Hamiltonian operator, i.e. an operator invariant under symmetry operations of the corresponding space group of the crystal. This invariance implies the concept of an ideal (perfect) crystal and cyclic boundary conditions (Bloch condition) in order to yield only one-dimensional irreducible representations of the translational group.

In the case of a molecule or isolated cluster, the final state  $\langle z | f \rangle$ , i.e. the wave function for the photoelectron, can be evaluated properly in terms of a multiple scattering approach as a continuum state of the initial state Hamiltonian operator by applying particular boundary conditions for  $|z| \rightarrow \infty$  [5-8].

This type of approach cannot be applied to solid state systems unless one considers a semi-infinite crystal, i.e. a crystal with a surface and a periodic potential function  $\langle z | V \rangle$  defined in a semi-open interval  $|\infty < z \leq 0|$ . In fact, such an approach was discussed by Liebsch [9] for the theory of photoemission from localized adsorbate levels. However, for a semi-infinite crystal the Bloch condition can no longer be applied three dimensionally. For a semi-infinite crystal the translational properties of the one-electron wave functions  $\langle z | i \rangle$  have to be classified in terms of Floquet's theorem (e.g. Cotterly [10]). Applying purely group theoretical considerations, the arguments are

fairly obvious [10]: if cyclic boundary conditions are not applied, the translations form an infinite Abelian group, for which not all irreducible representations are one-dimensional.

Though a semi-infinite crystal is definitely the best model to describe not only surface states but also photoionization experiments for solid state systems, it has the disadvantage that 1) information about the actual structure of the surface has to be available, and 2) the usual concept of band structure calculations is no longer applicable. Choosing therefore Bloch functions as initial states  $\langle z|i\rangle$ , assumptions have to be made about the final state  $\langle z|f\rangle$ . These assumptions are more or less crucial. However, since it is well believed that for X-ray photoemission experiments the final state is of less importance than the initial state, it seems that Bloch functions are still the most efficient tool to interpret X-ray photoelectron spectra (ESCA, XPS) for solid state systems.

Thus the interpretation of valence XPS for solid state systems is much more complex than in the case of soft X-ray emission spectra, where within the premises of Koopmans' theorem both the initial and the final state can be considered as bound one-electron eigenfunctions of the ground state crystal Hamiltonian operator.

According to the conceptual difficulties mentioned above, theoretical interpretations for relative intensities of XPS in terms of Bloch functions are inherently only qualitative.

## 2. Transition Probabilities

Suppose that the transition probability per unit time for the photoionization of the  $i$ th one-electron state  $\langle z|i\rangle$  (Bloch function) to a final state  $\langle z|f\rangle$  is given by

$$|M_{ij}|^2 \propto |\langle f|\nabla|i\rangle|^2 = (E_f - E_i)^{-2} |\langle f|\nabla V|i\rangle|^2. \quad (1)$$

Especially for a Hamiltonian operator  $H = -\nabla^2 + V$  of muffin tin form, as applied for many band structure calculations, the r.h.s. of (1) is very useful, since in the region of constant potential  $\nabla V = 0$ . However, if  $\langle z|f\rangle$  is not an eigenfunction of  $H$ , (1) is only an approximation to the square of the momentum matrix [11].

In the following a very simple model for the final state  $\langle z|f\rangle$  will be used, namely an outgoing spherical wave of the energy  $E_f = k^2 = \hbar\nu - (E_F - E_i) - E_A$ ,  $\hbar\nu$  being the energy of the incident photon source,  $E_F$  the Fermi energy and  $E_A$  the work function. No interactions to the neighbouring sites (back scattering) will be considered, because these interactions would imply boundary conditions, not compatible with the Bloch condition.

By assuming that according to (1)  $|M_{ij}|^2$  can be replaced by  $\langle f|\nabla V|i\rangle^2$ , only contributions of the atomic spheres, i.e. regions of spherical symmetric potential, have to be considered. However, in this case surface integrals have to be taken into account [12].

Let  $\Phi_i(\hat{z}_p)$  be a proper normalized eigenfunction of the Hamiltonian operator in sphere  $p$

$$\Phi_i(\hat{z}_p) = \sum_l c_{lm}(E_i) u_l(r_p, E_i) Y_{lm}(\hat{z}_p) \quad (2)$$

and  $\Phi_f(\hat{z}_p)$  an outgoing spherical wave

$$\Phi_f(\hat{z}_p) = 4\pi \sum_{lm} i^l j_l(kr_p) Y_{lm}(\hat{z}_p) Y_{lm}^*(\hat{k}) \quad k^2 = \hbar\omega - (E_F - E_i) - E_A. \quad (3)$$

Therein  $u_l(r_p, E_i)$  is the regular solution of the radial Schrödinger equation in sphere  $p$  for the eigenvalue  $E_i$  and angular momentum  $l$ ,  $j_l(kr_p)$  a spherical Bessel function and  $Y_{lm}(\hat{x})$  a spherical harmonic.

By averaging over all possible directions of  $k$ , the following formula for the transition probabilities can be obtained,

$$|M_{ij}|^2 \propto \sum_{p=1}^N \sum_l q_l^p(E_i) \lambda_l^p(E_i) \delta(E_F - E_i + E_A - k^2 + \hbar\omega) \quad (4)$$

where  $N$  is the total number of atomic spheres per unit cell,  $q_l^p(E_i)$  the  $l$ -like charge [13] in sphere  $p$  and  $\lambda_l^p(E_i)$  is given by

$$\lambda_l^p(E_i) = R_l^p(E_i)^{-1} \sum_{l'} (2l' + 1) \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} R_{l'l}^p(k^2, E_i)^2. \quad (5)$$

In (5)  $\begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}$  are Clebsch-Gordan coefficients,

$$R_l^p(E_i) = \int_0^{b_p} |u_l(r_p, E_i)|^2 r_p^2 dr_p, \quad (6)$$

$b_p$  being the  $p$ th atomic sphere radius, and

$$\begin{aligned} R_{l'l}^p(k^2, E_i) = & \frac{1}{2}(k^2 - E_i) \int_0^{b_p} j_{l'}(kr_p) u_l(r_p, E_i) r_p^3 dr_p - \frac{1}{2} b_p^2 j_{l'}(kb_p) u_l(b_p, E_i) \\ & - \frac{1}{2} b_p^3 [j_{l'}(kb_p) u_l'(b_p, E_i) - u_l(b_p, E_i) j_{l'}'(kb_p)] \\ & + (k^2 - E_i)^{-1} b_p^2 [j_{l'}'(kb_p) [2u_l'(b_p, E_i) + u_l(b_p, E_i) b_p^{-1}] \\ & - j_{l'}(kb_p) [2u_l''(b_p, E_i) + u_l'(b_p, E_i) b_p^{-1}]]. \end{aligned} \quad (7)$$

Therein  $u_l'(b_p, E_i)$ ,  $u_l''(b_p, E_i)$  and  $j_{l'}'(kb_p)$  are defined as follows

$$\begin{aligned} u_l'(b_p, E_i) &= \left. \frac{\delta u_l(r_p, E_i)}{\delta r_p} \right|_{r_p=b_p}; & u_l''(b_p, E_i) &= \left. \frac{\delta^2 u_l(r_p, E_i)}{\delta r_p^2} \right|_{r_p=b_p}; \\ j_{l'}'(kb_p) &= \left. \frac{\delta j_{l'}(kr_p)}{\delta r_p} \right|_{r_p=b_p}. \end{aligned} \quad (8)$$

The total transition probability per unit time is obtained by summing over all possible

occupied electronic states  $i$ . This transition probability will be proportional to the relative intensity  $I_0(E)$

$$\begin{aligned} I_0(E) &\propto \sum_i \left\{ \sum_{p,l} q_l^p(E_i) \lambda_l^p(E_i) \right\} \delta(E_F - E_i + E_A - k^2 + \hbar\omega) \\ &= \delta(E_F + E_A - E - k^2 + \hbar\omega) \sum_{p,l} \lambda_l^p(E) \sum_i q_l^p(E_i) \delta(E_i - E) \\ I_0(E) &\propto \delta(E_F + E_A - E - k^2 + \hbar\omega) \sum_{p,l} \lambda_l^p(E) \chi_l^p(E). \end{aligned} \quad (9)$$

In (9)  $\chi_l^p(E)$  is the so-called character density of states (local  $l$ -like partial density of states) as defined by Schwarz *et al.* [13, 14].

### 3. Broadening Effects

Broadening effects can be treated within one-electron theory only parametrically. Unfortunately, there is little known about these effects in the case of photoelectron spectra. In the present paper a broadening function of Lorentzian type

$$I_1(E) = \pi^{-1} I_0(E_i) \frac{\gamma(E) |2}{(E - E_i)^2 + \gamma^2(E) |4} \quad (10)$$

is applied. In (10)  $I_0(E_i)$  is the theoretical intensity (9) and  $\gamma(E)$  an energy-dependent half-width parameter

$$\gamma(E) = \gamma_0 + W \left( 1 - \frac{E - E_0}{E_F - E_0} \right)^2 \quad (11)$$

where  $\gamma_0$  corresponds to the line width of the (monochromatized) photon source and  $E_0$  to the bottom of the lowest valence band. The parameter  $W$  simulates valence broadening of the final state. This broadening function (10) is chosen in analogy to soft X-ray emission spectra [2, 15].

The intensity of photoelectron spectra depends largely on the line width of the incident photon source. In the present paper, for Al-K $\alpha$  a double focusing monochromator is assumed, providing an X-ray line width of 0.3 eV.

Finally, the intensity has to be corrected with respect to the spectrometer resolution, i.e. has to be folded with a spectrometer function. This spectrometer function is chosen to be again of Lorentzian type with a suitable half-width parameter  $S$ . The whole broadening procedure has the effect of smoothing the character density of states histograms [13].

### 4. The Valence X-Ray Photoelectron Spectrum of TiC

Two XPS of TiC have been published [16–18]. Unfortunately, the spectrum of Ihara *et al.* [16] seems to have a contamination peak, by which the ratio of peak heights is influenced. In Fig. 1 the reduced experimental spectrum (full line) of Hagström *et al.* [17, 18] (Al-K $\alpha$  photon source) is compared with three theoretical spectra, based on

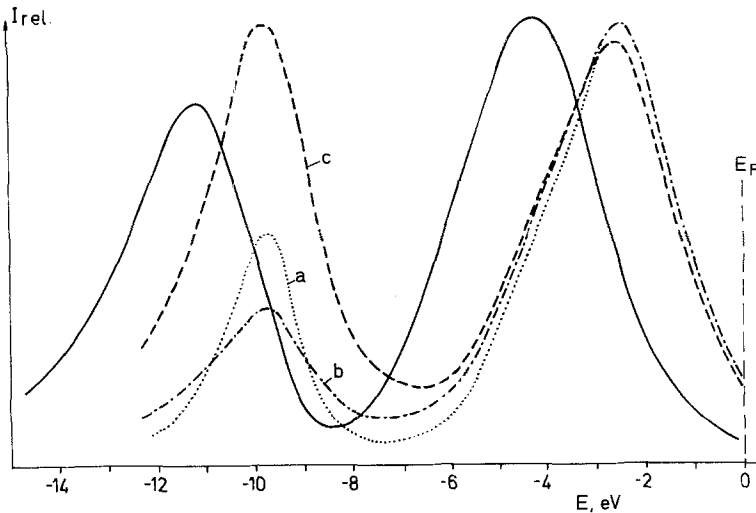


Fig. 1. The valence X-ray photoelectron spectrum of TiC. *a*) Density of states, folded with a spectrometer function ( $S = 1.0$  eV). *b*) Density of states, folded with an energy-dependent broadening function ( $\gamma_0 = 0.3$  eV,  $W = 1.5$  eV) and a spectrometer function ( $S = 1.0$  eV). *c*) Calculated intensity (9), folded with an energy-dependent spectrometer function ( $\gamma_0 = 0.3$  eV,  $W = 1.5$  eV) and a spectrometer function ( $S = 1.0$  eV). The full line refers to the reduced experimental spectrum of Hagström *et al.* [17, 18]

results of a self-consistent APW band structure calculation [13]. In particular these theoretical spectra correspond to

- a) the density of states, folded with a spectrometer function ( $S = 1.0$  eV);
- b) the density of states, folded with an energy-dependent broadening function ( $\gamma_0 = 0.3$  eV,  $W = 1.5$  eV) and a spectrometer function ( $S = 1.0$  eV);
- c) the calculated intensity, according to (9), folded with an energy-dependent broadening function ( $\gamma_0 = 0.3$  eV,  $W = 1.5$  eV) and a spectrometer function ( $S = 1.0$  eV).

For all theoretical spectra the calculated Fermi energy [13] is used.

As compared with spectrum *a*, the experimental spectrum shows a rather broad and intense peak in the vicinity of the band with predominantly Carbon *s*-character [13]. The experimental UV photoelectron spectra [17, 18] show that this band is successively built up, going from a Ne-I, He-I, He-II to an Al-K $\alpha$  photon source. This suggests that not only broadening effects but also the transition matrix elements are of some importance. The calculated intensity (spectrum *c*), based on a plane wave approximation for the photoelectron wave function, corrects to some extent the effect of transition matrix elements. However, in this case effects are overestimated.

The relative position of peaks for the theoretical spectra is in very good agreement with the experimental one. This shows that density of states functions and related quantities such as the character density of states can be used to predict the relative position of peaks. The ratio of relative intensities can be covered only qualitatively. However, it seems that spectrum *c*, based on (9), is a qualitative improvement as

compared with those theoretical spectra using uniform matrix elements [19], i.e. only the density of states.

Recalling all approximations used (dipole approximation, Koopmans' theorem, muffin-tin approximation, local exchange, final-state approximations, neglect of surface effects, broadening parameters) the theoretical results can be considered to be in good agreement with the experimental data.

The purpose of the present paper was to show that for an interpretation of valence X-ray photoelectron spectra of solid state systems, in the first place the density of states of the bulk can be used. In order to estimate trends of the transition matrix elements, simple final state approximations such as applied in (9) will be useful. However, one has to keep in mind the conceptual difficulties connected with both the initial and the final state.

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