Core and Valence Structures in $K\beta$ X-ray Emission Spectra of Chromium Materials

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ABSTRACT: We analyze the core and valence transitions in chromium in a series of materials with a number of different ligands and including the oxidation states: CrII, CrIII, CrIV, and CrVI. To study the core-to-core transitions we employ the CTMAXAS program and investigate the shapes, widths, intensities, and energy positions of the $K\beta_{1,3}$ and $K\beta'$ lines in each oxidation state. The theoretical spectra are compared with experimental data obtained with synchrotron radiation.

We found that the $K\beta_{1,3}$ peak shifts to higher energy with increasing spin state. In addition, the widths of the $K\beta_{1,3}$ peak increases as the oxidation state decreases, which we explain from the increased spread of the multiplet structures. In the $K\beta'$ structure the presence of two peaks in CrII, CrIII, and CrIV is due to the large 3p-3d exchange interaction. For the analysis of the valence transitions we utilize the DV-Xα method. We study the dependence of the relative intensities of the $K\beta''$ and $K\beta_{1,3}$ structures on symmetry, bond length, and the effective number of 3d and 4p electrons in different chemical environments.

1. INTRODUCTION

Chromium is extensively used in the chemical industry in applications such as metal plating, leather tanning, pigments, or anticorrosion coatings. When assessing the potential toxicity of chromium, the concept of speciation must be emphasized: CrIII is considered an essential micronutrient in the human diet. In contrast, CrVI is highly toxic and its compounds are considered human carcinogens. Therefore, the determination of chromium speciation in solid samples is critical for environmental and industrial purposes. Results have recently been published that evaluate the potential of the commercial wavelength-dispersive X-ray fluorescence spectrometer to perform practical quantitative speciation analysis of chromium in solid samples using CrKβ X-ray emission spectroscopy (XES).1

In recent years, much progress has been achieved in the interpretation of the Kβ X-ray emission spectrum of 3d transition metals.2–11 It has been known for a long time that Kβ emission spectra of 3d metals show a pronounced chemical sensitivity.12–15 Two different regions can be distinguished in the Kβ X-ray emission spectrum. The first region corresponds to the metal 3p core structure and consists of a Kβ1,3 main line and a lower energy small peak Kβ″. The second structure corresponds to valence structure and contains two satellite lines: Kβ″, directly below the Fermi level, and at lower energies Kβ′′ or crossover peak. Figure 1 shows the experimental spectra including a detailed assignment.

The Kβ″ feature at lower energy is due to the (3p,3d) exchange interaction. It has also been assigned to either collective excitations or charge-transfer processes.16,17 Photo-emission spectroscopy on free atoms, however, shows that intra-atomic interactions dominate the Kβ spectral shape.18,19 Some authors consider that the Kβ″ satellite line originates as the result of a double vacancy process in the presence of a 3d spectator-hole.20 Others believe it is the result of a plasmon excitation produced by a Kβ3 photon.21 However, it does not appear in metallic chromium. Alternatively, the Kβ″ peak has been assigned as ligand ns → metal 1s crossover transitions.22 The present work confirms that the crossover peak should be considered as metal np → metal 1s transitions, where the metal np orbital character mixes with the ligand 2s states.

According to theoretical calculations, the Kβ3 line is the s–d dipole forbidden transition when free atoms are considered,23,24 since the ΔI = ±1 condition is not satisfied. However, experimental data show a marked increase in the intensities of this line with the atomic number Z, and it is very strongly

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enhanced around $Z = 24$ (chromium). The origin of the $K\beta_1$ line is ascribed to transitions involving states that contain metal 3d character. In the chromium compounds 4p states are partly occupied, implying that $4p \rightarrow 1s$ transitions are possible (that correspond to the $K\beta_1$ line). Recently, Eeckhout et al. have demonstrated that Cr-3d states contribute very weakly to the $K\beta_{2,3}$ structure in chromium compounds.

The valence XES technique is suitable for analyzing otherwise challenging samples such as amorphous, nanocrystalline and heterogeneous materials. Lancaster et al. by means of the study of iron $K\beta$ valence XES of nitrogenase, demonstrated that these data provide a signature for the presence and identity of the central atom in this catalyst. The presence of Cr–C bonds in the bulk structure of electrochemically deposited amorphous chromium coatings was confirmed by means of this technique. Eeckhout et al. also have shown that a contaminated soil sample most probably contains Cr carbides and/or phosphides from anthropogenic origin.

The main objective of this work is to study the core and valence structures of $K\beta$ emission spectra in chromium materials with different oxidation states: $\text{Cr}^{II}$ (3$d^4$), $\text{Cr}^{III}$ (3$d^3$), $\text{Cr}^{IV}$ (3$d^2$), and $\text{Cr}^{VI}$ (3$d^0$). In order to study the core-to-core transitions we employ the CTM4XAS program and investigated the shapes, widths, intensities, and energy positions of the $K\beta_{1,3}$ and $K\beta''$ peaks in each oxidation state. To analyze the valence structure we utilize the DV-Xa method. In particular, we study the dependence of the relative intensities of $K\beta''$ and $K\beta_{1,3}$ satellite lines (with respect to the main $K\beta_{1,3}$ line) on symmetry, bond length, and effective number of 3d and 4p electrons in different chemical environments.

2. COMPUTATIONAL METHODS

The Cr $K\beta$ (1s 3p) core X-ray emission spectra were calculated with the charge transfer multiplet (CTM4XAS) program. CTM4XAS assumes that the intermediate state can be described with the relaxed 1s core hole state, as has been used in most published $K\beta$ calculations. It has been shown by Glatzel et al. that the intermediate state should be described as the 1s photoemission state. For metallic and covalent systems the 1s photoemission spectra is dominated by the peak related to the lowest energy excited 1s core hole state. In all, not-too-ionic systems where the 3d band is less than half-filled have the largest XPS intensity at their lowest energy excited 1s core state. An explicit calculation of the 1s photoemission spectrum of $\text{Cr}_2\text{O}_3$ shows that over 90% of the intensity is contained into a single peak related to the well-screened final state, which relates to a 1s 3d$^4$ final state. The ground state has a 3d$^5 + 3d^4 3p$ configuration with $4\Delta_2$ symmetry. The excitation of a 1s electron will create a lowest energy state that consists of the configuration 1s$^2$ 3d$^5 + 1s^1 3d^4 3p$ in which the symmetry of the 3d$^5$ part of the state remains $4\Delta_2$. This state will obtain most of the intensity, and because for $\text{Cr}_2\text{O}_3$, the charge transfer energy $\Delta$ is approximately equal to the Hubbard $U$, the lowest energy state is close to 50% 1s$^1$ 3d$^5$ and 50% 1s$^1$ 3d$^4$ 3p. In the case of very ionic systems this reasoning does not always work because the poorly screened peak can have more intensity as the well screened peak.

In all $\text{Cr}^{II}$, $\text{Cr}^{IV}$, and $\text{Cr}^{VI}$ materials, the weight of the well-screened peak will be higher than 90%. In the charge-transfer multiplet model, one starts with an atomic model. The ground state of a 3d transition-metal ion can be described as a 3d$^5$ configuration. When a 1s electron is excited to the continuum, the $K\beta$ emission spectrum can be calculated from the dipole transition matrix element for 1s$^2$ 3d$^5$ $\rightarrow$ 3p$^3$ 3d$^5$ calculations. In the calculations, the energy levels of the initial state and final states are calculated and the spectrum is simulated by evaluating the dipole transition matrix elements. The initial state is influenced by the 3d–3d Coulomb interaction and the 1s–3d exchange interaction. In the final state, the multiplet splitting is determined from the 3d–3d Coulomb interaction, the spin–orbit coupling of the 3p hole and the 3p–3d Coulomb and exchange interaction. In the ligand-field multiplet model the effects of neighboring atoms are introduced via the crystal field in both the initial state and final state.

The valence X-ray emission spectrum is calculated from the transition of the 1s core state to the occupied metal p-character. The occupied metal p-character is determined with the DV-Xa method. The crossover transitions are included in these calculations.
3. EXPERIMENTAL SECTION

Kβ emission spectra of CrVI and some compounds of CrIII and CrII were measured using a Johann-type spectrometer at the D12A-XRD1 beamline of the National Synchrotron Light Laboratory (LNLS), in Campinas, Brazil. The energy analysis of the fluorescence radiation was performed using a Si(333) analyzer with spherical focalization. The analyzer was scanned through the Kβ spectrum, including both the Kβ1,3 and the Kβ2,5 emission lines of Cr. Analyzer, detector, and sample were arranged on a Rowland circle of 0.42 m diameter. The whole spectrometer was mounted in a vacuum chamber in order to avoid intensity losses due to absorption in the air and to reduce the background intensity from scattering in the air. 6.1 keV monochromatic radiation was used to excite the samples. Measurements were carried out using conventional 45°−45° reflection geometry. The instrumental energy resolution was evaluated in 1.6 eV (Kβ1,3) and in 1.8 eV (Kβ2,5) at the energy of the CrKβ1,3 line. The spectrometer was calibrated using the Kβ1,3 peak from a pure Cr sample. Its position was set to the energy value given by Bearden (5946.71 eV). The sample holder was designed in such a way that the illuminated area on the sample is tangent to the Rowland circle at the same point for each sample. Stability and repeatability of the spectrometer was checked throughout the experiments by measuring the position of the Kβ1,3 peak of Cr metal. Part of the experimental data was published elsewhere \(^ {3,37,38}\).

4. RESULTS

Figure 1 shows an important dependence between the valence structure and oxidation state of chromium. In particular, the Kβ1 and Kβ2,5 satellite lines have higher intensity in CrVI with respect to CrIII. The Kβ2,5 lines are broader in CrIII, and their energies are around 5985 eV, whereas for CrVI are close to 5990 eV. The energy shift of the Kβ2,5 line with respect to the same line in CrVI is more sensitive to the oxidation state than shift of the Kβ1,3 line.\(^ {3}\)

A. Analysis of the Kβ1,3 Line. Figure 2a,b shows theoretical and experimental results, respectively, of the core spectra. The theoretical calculations for CrIII, CrIV, and CrV have been performed with atomic values for the Slater integrals and the spin−orbit couplings, combined with a crystal field value of 0.6 times the formal valence. In these figures it is observed that the Kβ1,3 peak position shifts to lower energies as the oxidation state increases. In experiment, the CrIII peak is positioned at 5950 eV and the CrVI peak at 5946 eV. In the calculations the shift is from 5951 eV (CrIII peak) to the CrVI peak at 5947 eV. It is noted that the Kβ' structure has two peaks for CrII, CrIII, and CrIV (Figure 2a).

In Figure 2a,b, it is observed that the Kβ1,3 line of CrIII has a weak shoulder on the low energy side. This shoulder arises from a spin flip in the metal valence shell.\(^ {31}\)

B. Analysis of the Valence XES Spectra. Table 1 shows the Cr compounds and the clusters used to perform the calculations with the DV-Xα method. In each cluster, the central atom of Cr is surrounded by 4 or 6 ligand atoms organized in tetrahedral (Td) and octahedral (Oh) symmetry, respectively. In the theoretical calculations, 1s−4p atomic orbitals have been used as basis functions for chromium, 1s−2p orbitals were used for oxygen, and 1s−3d were used for chlorine. Slater’s exchange parameter was taken to be α = 0.7 in all cases.

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Table 1. Compounds Used for Calculations

<table>
<thead>
<tr>
<th>compounds</th>
<th>oxidation state</th>
<th>symmetry</th>
<th>cluster</th>
<th>bond length a (Å)</th>
<th>ref</th>
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</thead>
<tbody>
<tr>
<td>CaCrO₄</td>
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<td>Td</td>
<td>[CrO₄]²⁻</td>
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<td>39</td>
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<tr>
<td>Cr₂O₄</td>
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<td>Td</td>
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<td>39</td>
</tr>
<tr>
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<td>43</td>
</tr>
<tr>
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<td>Td</td>
<td>[CrO₄]²⁻</td>
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<td>44</td>
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<tr>
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<td>Oh</td>
<td>[CrO₆]³⁻</td>
<td>2.00</td>
<td>41</td>
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<td>Oh</td>
<td>[CrO₆]³⁻</td>
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<tr>
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<td>Oh</td>
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<td>2.05</td>
<td>44</td>
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<tr>
<td>Rb₂[CrCl₄]₂</td>
<td>2</td>
<td>Oh</td>
<td>[CrCl₄]²⁻</td>
<td>2.35</td>
<td>42</td>
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<tr>
<td>Rb₂[CrCl₄]₂</td>
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<td>Oh</td>
<td>[CrCl₄]²⁻</td>
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<td>43</td>
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<td>CrCl₂</td>
<td>2</td>
<td>Oh</td>
<td>[CrCl₄]²⁻</td>
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<td>44</td>
</tr>
<tr>
<td>CrCl₂</td>
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<td>Oh</td>
<td>[CrCl₄]²⁻</td>
<td>2.55</td>
<td>45</td>
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</table>
Figure 3 shows the comparison between theoretical and experimental Cr$K\beta$ spectra: (a) [CrO$_4$]$^{2-}$ with $T_d$ symmetry corresponding to K$_2$CrO$_4$; (b) [CrO$_6$]$^{9-}$ with $O_h$ symmetry corresponding to Cr$_2$O$_3$; (c) [CrCl$_6$]$^{3-}$ with $O_h$ symmetry corresponding to CrCl$_3$. The theoretical spectra were shifted to align to the maximum of peak of the measured $K\beta_{2,5}$ emission. A Gaussian broadening of 1.0 eV was used.

5. ANALYSIS AND DISCUSSION

A. Core XES Spectra. It is known that the core emission is sensitive to the metal spin state. More exactly, it reflects the effective number of unpaired metal 3d electrons. The shift of the $K\beta_z$ line is not caused by a change in nuclear screening between different oxidation states but by variations in the exchange splitting, i.e., the $K\beta_{1,3}$ line position depends on the...
exchange interaction between the core hole and the unpaired spin in the valence shell as can be seen for the theoretical results found for the different oxidation states of Cr (see the inset in Figure 2a). Glatzel et al.31 and Glatzel and Bergmann3 found a similar behavior for Mn fluorides and oxides measured after photoionization.

In addition, the widths of the Kβ1,3 line increases as the oxidation state decreases (see Figure 2a,b), because the multiplet structures are spread over a larger energy. In particular, as CrII is the d4 high-spin state then this oxidation state has the widest Kβ1,3 structure and largest shift to higher energy.

Table 3 shows the terms of the final states that contribute mainly to the intensity of the peaks which were obtained with the CMT4XAS program. For example, the lowest energy 1s1 3d4 state of CrII has a 4D configuration and its main 3d4 component is 5D, i.e., equivalent to the ground state. Because the main contribution is the same every time as the ground state, these peaks behave similarly if a crystal field is applied, i.e., they are not sensitive to change of the ligand-field splitting (10Dq). The intensity of the peaks changes if the 3p3d multiplet effects are modified (cf. Figure 2a).

### B. Valence XES Spectra.

With the purpose of studying how the relative intensities of the Kβ″ and Kβ2,5 satellite lines are related to effective number of 3d (N3d) and 4p (N4p) electrons and bond length (l), an elemental multivariate statistical analysis method was used. The degree of linear relationship for N pairs of data \((x_i, y_i)\), \(i = 1, N\) can be measured through the following correlation coefficient:

\[
r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{N \sum x_i^2 - (\sum x_i)^2}} \frac{\sqrt{N \sum y_i^2 - (\sum y_i)^2}}{\sqrt{t}}
\]

The \(r\) value is between 0 (when there is no correlation) and ±1 (when \(y_i\) can be expressed as a linear function of \(x_i\)). \(x_i\) (l, \(N_{3d}\) and \(N_{4p}\)) were considered to be the parameters of the compound, and the \(y_i\) were considered to be the relative intensity of the Kβ″ and Kβ2,5 lines. The values of \(N_{3d}\) and \(N_{4p}\) l, and the theoretical relative intensities used in the calculations are shown in Table 4. The numbers of the effective electrons

| cluster oxidation state symmetry MO Cr-3p Cr-3d Cr-4p O-2s O-2p |
|-----------------|----------|----------|----------|----------|----------|
| \([\text{CrO}_4]^{-2}\) | \(T_d\) | 3\(t_2\) 98.72 0.04 0.60 0.65 | 4\(t_2\) 0.73 3.08 1.77 93.72 0.70 | 5\(t_2\) 0.09 37.73 0.02 3.01 59.15 | 1\(e\) 0.00 0.00 40.41 0.00 0.00 | 6\(t_2\) 0.30 0.65 5.44 0.66 92.95 |
| \([\text{CrO}_6]^{-2}\) | \(O_h\) | 3\(t_{1u}\) 99.26 0.05 0.21 0.28 | 4\(t_{1u}\) 0.19 0.06 1.02 97.17 0.12 | 5\(t_{1u}\) 0.56 0.05 4.50 0.51 94.43 | 6\(t_{1u}\) 0.10 0.05 0.56 0.95 98.39 | 2\(t_{2g}\) 0.02 0.02 0.21 0.02 5.73 |
| \([\text{CrO}_6]^{-2}\) | \(O_h\) | 3\(t_{2g}\) 0.05 0.05 0.46 0.65 98.84 | 4\(t_{2g}\) 0.11 0.05 0.91 97.64 0.15 | 5\(t_{2g}\) 0.21 0.10 5.20 0.22 94.37 | 6\(t_{2g}\) 0.05 0.05 0.46 0.65 98.84 | 2\(t_{2g}\) 0.02 0.02 0.21 0.02 5.73 |

**Table 3. Principal Terms That Contribute to the Intensity of Kβ″**

<table>
<thead>
<tr>
<th>AO (%)</th>
<th>Cr-3p</th>
<th>Cr-3d</th>
<th>Cr-4p</th>
<th>O-2s</th>
<th>O-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrII</td>
<td>4D(5D)</td>
<td>4F(5D)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrIII</td>
<td>3F(4F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrIV</td>
<td>2F(3F)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

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(\(N_{3d}\) and \(N_{4p}\)) were calculated by Mulliken’s population analysis using the DV-Xa method.

The correlation coefficient between the relative intensity of \(K\beta^0\) peak (\(IK\beta^0/IK\beta_{1,3}\)) and the bond length \(l\) for Cr–O compounds is \(r = -0.83\). This correlation coefficient indicates that there is a correlation between these parameters but that is not linear (see Figure 4), which agrees with the decreasing exponential trend found by Fazinić et al.\(^7\)

Then, the correlation between the relative intensities and \(l\) was analyzed in another way. Compounds were separated by ligand (O and Cl) and by symmetry (\(T_d\) or \(O_h\)). The results are shown in Table 5. The bond length \(l\) was found to be linearly correlated with the \(IK\beta^0/IK\beta_{1,3}\) and \(IK\beta_{2,5}/IK\beta_{1,3}\) relative intensities of Cr–Cl compounds, with a negative slope; the bond length \(l\) was also found to be linearly correlated with \(IK\beta_{2,5}/IK\beta_{1,3}\) of Cr–O compounds in the two symmetries, with a negative slope.

![Figure 4. Relative intensities of the \(K\beta^0\) structure in relation to the \(K\beta_{1,3}\) peak. Solid circles: Cr–O compounds with \(T_d\) symmetry; open circles: Cr–Cl compounds with \(O_h\) symmetry; solid squares: Cr–Cl compounds. The exponential fit (in red line) to the Cr–O data is \(1800 \times e^{(-3.855)} = 0.25\), \(R^2 = 0.998\); and to the Cr–Cl data is \(8500 \times e^{(-4.003)} = 0.03\), \(R^2 = 0.992\).](Image)

<table>
<thead>
<tr>
<th>compound</th>
<th>oxidation state</th>
<th>symmetry</th>
<th>(IK\beta^0/IK\beta_{1,3})</th>
<th>(IK\beta_{2,5}/IK\beta_{1,3})</th>
<th>(N_{3d})</th>
<th>(N_{4p})</th>
<th>(l) (Å)</th>
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<tr>
<td>CaCrO₄</td>
<td>6</td>
<td>(T_d)</td>
<td>3.88</td>
<td>4.94</td>
<td>3.52</td>
<td>0.39</td>
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<td>K₂CrO₄</td>
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<td>(T_d)</td>
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<td>3.56</td>
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<td>3.98</td>
<td>3.59</td>
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<tr>
<td>CaCrCl₄</td>
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<td>(T_d)</td>
<td>1.78</td>
<td>3.29</td>
<td>3.66</td>
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<td>Cr₂O₂</td>
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<td>(O_h)</td>
<td>0.98</td>
<td>4.04</td>
<td>3.48</td>
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<td>Na₃CrCl₆</td>
<td>3</td>
<td>(O_h)</td>
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<td>CuCrO₂</td>
<td>3</td>
<td>(O_h)</td>
<td>0.69</td>
<td>3.41</td>
<td>3.85</td>
<td>0.35</td>
<td>1.99</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>3</td>
<td>(O_h)</td>
<td>0.66</td>
<td>3.40</td>
<td>3.85</td>
<td>0.36</td>
<td>2.00</td>
</tr>
<tr>
<td>Cr</td>
<td>2</td>
<td>(O_h)</td>
<td>0.52</td>
<td>2.97</td>
<td>4.41</td>
<td>0.28</td>
<td>2.05</td>
</tr>
<tr>
<td>Cs₂[Cr₂Cl₆]</td>
<td>3</td>
<td>(O_h)</td>
<td>0.65</td>
<td>3.50</td>
<td>4.20</td>
<td>0.65</td>
<td>2.35</td>
</tr>
<tr>
<td>Na₂[CrCl₆]</td>
<td>3</td>
<td>(O_h)</td>
<td>0.64</td>
<td>3.44</td>
<td>4.21</td>
<td>0.64</td>
<td>2.36</td>
</tr>
<tr>
<td>CrCl₃.6H₂O</td>
<td>3</td>
<td>(O_h)</td>
<td>0.61</td>
<td>3.35</td>
<td>4.21</td>
<td>0.63</td>
<td>2.38</td>
</tr>
<tr>
<td>Rb₂[CrCl₆]</td>
<td>2</td>
<td>(O_h)</td>
<td>0.34</td>
<td>2.38</td>
<td>4.57</td>
<td>0.42</td>
<td>2.52</td>
</tr>
<tr>
<td>CrCl₂</td>
<td>2</td>
<td>(O_h)</td>
<td>0.27</td>
<td>2.11</td>
<td>4.58</td>
<td>0.39</td>
<td>2.55</td>
</tr>
</tbody>
</table>

Table 5. Correlation Coefficients \((r)\) between \(l\) and Relative Intensities of \(K\beta^0\) and \(K\beta_{2,5}\) Peaks

<table>
<thead>
<tr>
<th>ligand</th>
<th>symmetry</th>
<th>(r) ((l) vs (IK\beta^0/IK\beta_{1,3}))</th>
<th>(r) ((l) vs (IK\beta_{2,5}/IK\beta_{1,3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>(T_d)</td>
<td>-0.94</td>
<td>-0.99</td>
</tr>
<tr>
<td>O</td>
<td>(O_h)</td>
<td>-0.94</td>
<td>-0.99</td>
</tr>
<tr>
<td>Cl</td>
<td>(O_h)</td>
<td>-1</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

In Table 6 an almost linear relationship (i.e., \(r\) is very close to \(-1\)) could be observed to exist between \(IK\beta^0/IK\beta_{1,3}\) and \(N_{3d}\) for Cr–Cl compounds, and also between \(IK\beta_{2,5}/IK\beta_{1,3}\) and \(N_{3d}\) for Cr–O compounds with \(T_d\) symmetry. In the first case, where the \(N_{3d}\) influences on \(IK\beta^0/IK\beta_{1,3}\), this behavior can be explained by considering that the valence AOs of the Cl⁻ ion (Cl-3s and Cl-3p) have a larger radius than valence AOs O-2s and O-2p of the O²⁻ (\(r_{O^2-} = 181\) pm and \(r_{O} = 140\) pm); consequently, the first result is more affected by the 3d valence electrons of the Cr atom. In the second case, \(N_{3d}\) plays a very important role in the \(K\beta_{2,5}\) structure, since there is a covalent bond between Cr-3d and O-2p electrons in compounds with \(T_d\) symmetry.

A linear relationship with positive slope was found between \(IK\beta_{2,5}/IK\beta_{1,3}\) and \(N_{4p}\) for Cr–Cl compounds. This behavior is due to the fact that a larger Cr-4p population participates in the \(K\beta_{2,5}\) structure when a Cr–Cl bond occurs (with respect to a Cr–O bond), probably due to the size difference in the radius of the valence AOs on the two ligand atoms.

Therefore, if correlation coefficients for \(l\), \(N_{3d}\), and \(N_{4p}\) parameters are compared (Tables 5 and 6), the bond length would be the most appropriate parameter to analyze the relative intensities \(IK\beta_{2,5}/IK\beta_{1,3}\), since it is near \(-1\), irrespective of the ligand and the symmetry (see last column in Table 5). The numbers of \(N_{3d}\) and \(N_{4p}\) electrons are good correlation parameters, although it did not turn out to be that general.

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Figure 4 shows that the intensities of the $K\beta''$ line are higher in the compounds with $T_d$ symmetry than in those with $O_h$ symmetry. This behavior is due to the existence of covalent Cr–O bonds producing a lower bond length, and thus greater interaction between the valence orbitals, resulting in increased transition probabilities for this transition.

This figure further shows that the relative intensities of the $K\beta''$ line vary continuously for Cr–O compounds when the symmetry is changed from $T_d$ to $O_h$. This continuity is due to the participation of O-2s in both MOs; the participation of O-2s in both MOs is approximately 94% and 97%, respectively (Table 2).

In the $K\beta''$ structure for Cr–Cl compounds, the electron transition that generates the $K\beta''$ satellite line now originates from the $7t_{1u}$ MO, mainly formed by the Cl-3s. Therefore, the Cr–Cl compounds do not continue the same decreasing exponential trend, but rather show a different trend in Figure 4.

In Figure 5 theoretical relative intensities $\Delta K\beta_{2,5}/\Delta K\beta_{1,3}$ are shown in relation to the bond length. These results reveal three different trends: the first one corresponds to Cr–O compounds with $T_d$ symmetry; the second one corresponds also to Cr–O compounds but with $O_h$ symmetry, and the third one, to Cr–Cl compounds.

The $K\beta_{2,5}$ satellite line originates in $1e$, $5t_{2g}$, $6t_{2} \rightarrow 1a_1$ transitions, and in particular for CrO$_3$, the contributions are 0.21% ($1e \rightarrow 1a_1$), 0.45% ($5t_{2} \rightarrow 1a_1$) and 2.57% ($6t_{2} \rightarrow 1a_1$). If we add them up, we obtain the relative intensity of the $K\beta_{2,5}$ line, which is 3.23% and is shown in Figure 5 for the bond length of CrO$_3$ ($l = 1.80$ Å). In Figure 5 this oxide has smaller relative intensity of the $K\beta_{2,5}$ line of Cr–O (Figure 4) compounds. The $1e$ and $5t_{2}$ MOs are formed by Cr-3d and O-2p, allowing quadrupole and dipole transitions which contribute to the $K\beta_{2,5}$ line. The small contributions of these MOs, which are observed in Figure 3a, are characteristics of clusters with $T_d$ symmetry, and are due to a ~60% contribution of O-2p in both MOs (Table 2). The contribution of the $6t_{2}$ MO, instead, is more intense than the previous due to the fact that there is a major contribution from O-2p (92.95%) in this MO; there is also a minor participation of Cr-4p (see Table 2).

The [CrO$_4$]$^{2-}$ cluster of the CrO$_4$ oxide presents $O_h$ symmetry, and mainly the relative intensity of the $K\beta_{2,5}$ satellite line originates in the $5t_{1u} \rightarrow 1a_1g$ transitions. Since the cluster has $O_h$ symmetry, there is also a small contribution to the relative intensity from the $2t_{2g}$ MO. The values of contributions are 3.01% ($5t_{1u} \rightarrow 1a_1g$), 0.85% ($6t_{1u} \rightarrow 1a_1g$), and 0.13% ($2t_{2g} \rightarrow 1a_1g$), respectively. The sum of those values results in the relative intensity of the $K\beta_{2,5}$ line, which is 4.04% and is shown in Figure 5 for the bond length of Cr$_2$O$_3$ ($l = 1.90$ Å). In Figure 5 this oxide has higher relative intensity of the $K\beta_{2,5}$ line of Cr–O ($O_h$) compounds. The largest contribution to the relative intensity from the $5t_{1u}$ MO is characteristic of this type of symmetry in the Cr–O compounds, and it is due to the major participation (95.31%) of the O-2p AO. In addition, Cr-4p has a greater participation in the formation of this MO, as compared to the case of the $T_d$ cluster in the previous paragraph (2t$_{2g}$ MO), generating a greater dipole transition probability (see Table 2). The less contribution of the $6t_{1u}$ MO to the $K\beta_{2,5}$ intensity, in relation to the $5t_{1u}$ MO, is due to a smaller participation of the Cr-4p.

In the $2t_{2g}$ MO the $O$-2p participation is lower with respect to $5t_{1u}$ and $6t_{1u}$ MOs, generating a lower dipolar transition probability. In addition, there is a quadrupole contribution to the intensity of the $K\beta_{2,5}$ line, due to greater participation of the Cr-3d and O-2p AOs, which is according to the calculations performed by Eechout et al. using the FEFF8.2 code.

Then, we found that the intensities of the $K\beta_{2,5}$ line, which originate mainly in transitions from the $6t_{2}$ and $5t_{1u}$ MOs, are mostly formed by O-2p in the two symmetries, $T_d$ and $O_h$, respectively. In addition, the results of the Mulliken population analysis show that the major contribution of O-2p in clusters with $T_d$ symmetry corresponds to the $p_x$ and $p_z$ components. While for clusters with $O_h$ symmetry, the only contribution is from the $p_z$ component; in this way, $K\beta_{2,5}$ oscillator strength comes mainly from O-2p. Therefore, the discontinuity observed in Figure 5 for Cr–O compounds, is due to $5t_{1u}$ MO is formed entirely by O-2p.

The third trend for the higher $l$ values in Figure 5 corresponds to the Cr–Cl compounds. This trend appears because the transition that generates the $K\beta_{2,5}$ line now originates from the Cl-3p, which mostly participates in the formation of the $8t_{1u}$ MO.

As shown in Figure 5, the relative intensities of the $K\beta_{2,5}$ lines in the Cr–Cl compounds, for the smallest $l$ values, are similar to those of the Cr–O compounds, even when the bond length is higher than in the first ones. This is due to two reasons: in the first place, because of the larger size of Cl-3p as compared to O-2p; and in the second place, because of the larger contribution of the Cr-4p in the $8t_{1u}$ MO in relation to the $5t_{1u}$ of the Cr–O compounds (see Table 2).

6. CONCLUSIONS

Core and valence structures of the Cr $K\beta$ X-ray emission spectra were studied theoretically and compared with experimental spectra. The calculations of core structure ($K\beta''$ and $K\beta_{1,3}$ peaks) were performed with the CTM4XAS 5.5 program, and for valence structure ($K\beta''$ and $K\beta_{2,5}$ peaks) with the DV-Xa method. The main results are summarized below:

We found for Cr compounds that the $K\beta_{1,3}$ peak shifts to higher energy when spin state increased (i.e., when oxidation...
states decrease). Besides, the theoretical and experimental widths of the Kβ\textsubscript{12.3} increases as the oxidation state decreases because the multiplet structures are spread over a larger energy.

In the Kβ\textsuperscript{0} structure the presence of two peaks in Cr\textsuperscript{II}, Cr\textsuperscript{III}, and Cr\textsuperscript{IV} is due to large 3p3d multiplet effects (including the exchange) which create multiple states with the same symmetry as the ground state (see Table 3). Besides, we found that the intensity of Kβ\textsuperscript{0} structure increases as the oxidation state decreases, because the 3p multiplet effects increase.

The differences in both experimental and theoretical energies among the Kβ\textsubscript{12} and Kβ\textsuperscript{0} lines for the Cr−O compounds are 16 and 14 eV, respectively. These values are very near the orbitals of O (15 eV). This decreases, because the multiplet structures are spread over a larger energy.

The existence of a covalent bond in the Cr−O−Cr compounds is due to the fact that the Cr−O−Cr compound is a non-linear molecule. The dihedral angle between the Cr−O−Cr planes is 16 and 14 eV, respectively. These values are very near the orbitals of O (15 eV). This decreases, because the multiplet structures are spread over a larger energy.

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■ REFERENCES


