CHEMICAL EFFECTS ON THE $K_\beta/K_\alpha$ INTENSITY RATIOS IN FIRST-ROW TRANSITION ELEMENT COMPOUNDS

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Chemical effects on the $K_\beta/K_\alpha$ X-ray intensity ratios for some first-row transition element compounds were studied experimentally and calculated. The vacancies in the $K$ shell were created by 59.5 keV $\gamma$ rays from an $^{241}$Am radioactive source and characteristic X-ray radiation from sample was measured by using Si(Li) and Ge(Li) detectors. The calculations were carried out using Brunner's model. The calculated relative $K_\beta/K_\alpha$ X-ray intensity ratios are in good agreement with the present and the previously published experimental data.

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1. Introduction

The study of the influence of chemical environment on the characteristic X-rays is of great importance for atomic physics and applied research. Therefore, the dependence of relative intensities in X-ray emission spectra on the chemical surroundings of emitted atom and excitation mode has been the subject of extensive experimental and theoretical investigation [1–28].

Earlier results concerned with the chemical environment which affect the $K_\beta/K_\alpha$ X-ray intensity ratios in coordination compounds of 3d elements and some other compounds are summarised in Table I. In compounds the chemical effects are interpreted in terms of valence electron distribution and chemical bonding. In the recent years, we measured the $K_\beta/K_\alpha$ X-ray intensity ratios for 3d elements...
TABLE I

Earlier studies on chemical effects.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mode of excitation</th>
<th>Dependence of $K_\beta/K_\alpha$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d$ elements</td>
<td>Electron capture and</td>
<td>few percent</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>photoionisation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3d$ elements</td>
<td>PIXE and XRF</td>
<td>up to 5%</td>
<td>[23]</td>
</tr>
<tr>
<td>Mn compounds</td>
<td>Photon excitation</td>
<td>up to 10%</td>
<td>[27]</td>
</tr>
<tr>
<td>$3d$ elements</td>
<td>Photon excitation</td>
<td>up to 5%</td>
<td>[5]</td>
</tr>
<tr>
<td>Ag and Mo</td>
<td>Photon excitation</td>
<td>No deviation as expected for $4d$ elements</td>
<td>[5]</td>
</tr>
<tr>
<td>Fe and Mn</td>
<td>Electron capture and</td>
<td>up to 10%</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>photoionisation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti,Cr,Mn</td>
<td>Electron impact ionisation</td>
<td>up to 6%</td>
<td>[16]</td>
</tr>
<tr>
<td>Cr and Mn</td>
<td>Photon excitation</td>
<td>Compounds with $T_d$ symmetry are generally larger than those</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with $O_h$ symmetry</td>
<td></td>
</tr>
<tr>
<td>$3d$ elements</td>
<td>Photon excitation</td>
<td>up to 9%</td>
<td>[25]</td>
</tr>
<tr>
<td>Cr,Mn,Co,Cu</td>
<td>Photon excitation</td>
<td>1–16%</td>
<td>[17]</td>
</tr>
<tr>
<td>Ti,V,Fe</td>
<td>Photon excitation</td>
<td>1–12%</td>
<td>[19]</td>
</tr>
<tr>
<td>Se,Br,Zr,Ce</td>
<td>Photon excitation</td>
<td>The smallest deviation</td>
<td>[19]</td>
</tr>
<tr>
<td>$3d$ elements</td>
<td>Photon excitation</td>
<td>Compounds with $T_d$ symmetry are generally larger than those</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with $O_h$ symmetry</td>
<td></td>
</tr>
<tr>
<td>Cr,Mn,Fe</td>
<td>Radioactive decay and</td>
<td>4%</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>photon excitation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs,Ba</td>
<td>Radioactive decay and</td>
<td>The smallest deviation</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>photon excitation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{51}$Cr labelled</td>
<td>Electron capture decay</td>
<td>up to 12%</td>
<td>[4]</td>
</tr>
<tr>
<td>compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{51}$Cr and $^{51}$Mn</td>
<td>Electron capture decay</td>
<td>5–10%</td>
<td>[12]</td>
</tr>
<tr>
<td>Ti</td>
<td>Electron impact ionisation</td>
<td>4%</td>
<td>[10]</td>
</tr>
<tr>
<td>$^{51}$Cr doped solids</td>
<td>Electron capture decay</td>
<td>Difference between compounds before and after annealing ranging from 2 to 3%</td>
<td>[15]</td>
</tr>
<tr>
<td>Cu alloys</td>
<td>Photon excitation</td>
<td>up to 3%</td>
<td>[28]</td>
</tr>
<tr>
<td>CrNi and CrAl</td>
<td>Photon excitation</td>
<td>up to 3.5%</td>
<td>[21]</td>
</tr>
</tbody>
</table>

both in pure elements and in various chemical compounds and alloys using a Ge(Li) and Si(Li) detector systems [17–21].

In the reported values of $K_\beta/K_\alpha$ X-ray intensity ratios of $3d$ elements and their compounds, the deviations in the results from pure element and from com-
pounds are ranging from 3 to 16%. These deviations were attributed to variations in the number of valence electrons [17], coordination number, and absorption effects of the ligands [18]. Furthermore, we observed that deviations 1–16% for 3d elements [19] are much larger than those for high Z elements (1–4%). Moreover, it was found that for first-row transition elements the \( K_\beta/K_\alpha \) X-ray intensity ratio depended on the mode of excitation [20]. Recently, we have measured the \( K_\beta/K_\alpha \) X-ray intensity ratios in different \( \text{Cr}_x\text{Ni}_{1-x} \) and \( \text{Cr}_x\text{Al}_{1-x} \) alloys [21] and found that they differed up to 3.5% between alloys with different concentration.

Band et al. [22] carried out the scattered wave \( \text{X}\alpha \) molecular orbital calculations for some chromium and manganese compounds and evaluated the relative change in the \( K_\beta/K_\alpha \) X-ray intensity ratios. Brunner et al. [23] proposed that the change in the \( K_\beta/K_\alpha \) X-ray intensity ratios was caused by the change in the screening of 3p electrons due to delocalization of the 3d electrons and estimated the difference between two chemical compounds in a simple model. Mukoyama et al. [24] estimated the chemical effect on the \( K_\beta_2/K_\alpha \) ratio for some Tc and Mo compounds using Brunner’s model. Furthermore, Raghavaiah et al. [25] calculated relative \( K_\beta/K_\alpha \) X-ray intensity ratios for some 3d elements using Brunner’s model and compared these with experimental data. The calculated values were found to be consistent with experimental results.

In the present work, \( K_\beta/K_\alpha \) X-ray intensity ratios for some 3d elements were measured and calculated by using Brunner’s model.

2. Computational method

According to Brunner, 3p orbitals suffer a contraction due to the altered screening of 3p orbitals by 3d orbitals charge delocalization in chemical bonding. The relative \( K_\beta/K_\alpha \) emission rate is given by

\[
\frac{(K_\beta/K_\alpha)_A}{(K_\beta/K_\alpha)_B} = \frac{1 + V_A}{1 + V_B},
\]

where \((K_\beta/K_\alpha)_i\) is the \( K_\beta/K_\alpha \) intensity ratio for the \( i \)-th chemical compound; \( V_i \) is relative deviation described as \( V_i = S_z C_{\text{eff}} K_d \). \( S_z \) is the sensitivity of 3p contraction to a 3d charge delocalization [23]. The values of \( S_z \) for 3d elements were computed by Brunner et al. [23] using the Dirac–Fock–Slater potential. The valence charge difference \( C_{\text{eff},i} \) is evaluated from the Pauling electronegativity concept as follows:

\[
C_{\text{eff},i} = V_f \left\{ 1 - \exp\left[-\left(X_A - X_B\right)^2/4\right]\right\},
\]

where \( V_f \) is formal oxidation number of the parent atom and \( X_A \) and \( X_B \) are the Pauling electronegativities [29] for atom \( A \) and \( B \) forming chemical bonding and \( K_d \) is the share of \( C_{\text{eff}} \). Brunner et al. used 0.52 for \( K_d \), for the transition elements. The calculated values of \( K_\beta/K_\alpha \) ratios are given in Table II.
Relative $K_\beta/K_\alpha$ X-ray intensity ratios. ON — oxidation number.

<table>
<thead>
<tr>
<th>Relative intensity ratios</th>
<th>$C_{eff,1}/C_{eff,2}$</th>
<th>Present studies</th>
<th>Earlier studies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc. values</td>
<td>Exp. values</td>
</tr>
<tr>
<td><strong>Mn/KMnO$_4$</strong></td>
<td>0/7</td>
<td>0.000/4.424</td>
<td>0.925</td>
</tr>
<tr>
<td><strong>Mn(NO$_3$)$_2$ · H$_2$O/KMnO$_4$</strong></td>
<td>2/7</td>
<td>0.121/4.424</td>
<td>0.927</td>
</tr>
<tr>
<td><strong>MnSO$_4$ · H$_2$O/KMnO$_4$</strong></td>
<td>2/7</td>
<td>0.442/4.424</td>
<td>0.933</td>
</tr>
<tr>
<td><strong>Mn(CO$_3$)/KMnO$_4$</strong></td>
<td>2/7</td>
<td>0.442/4.424</td>
<td>0.933</td>
</tr>
<tr>
<td><strong>MnBr$_2$/KMnO$_4$</strong></td>
<td>2/7</td>
<td>0.689/4.424</td>
<td>0.937</td>
</tr>
<tr>
<td><strong>MnCl$_2$ · 4H$_2$O/KMnO$_4$</strong></td>
<td>2/7</td>
<td>0.860/4.424</td>
<td>0.939</td>
</tr>
<tr>
<td><strong>MnCl$_2$ · 4H$_2$O/Mn(NO$_3$)$_3$ · 9H$_2$O</strong></td>
<td>2/2</td>
<td>0.860/0.121</td>
<td>1.012</td>
</tr>
<tr>
<td><strong>MnCl$_4$/KMnO$_4$</strong></td>
<td>4/7</td>
<td>1.720/4.424</td>
<td>0.954</td>
</tr>
<tr>
<td><strong>MnO$_2$/KMnO$_4$</strong></td>
<td>4/7</td>
<td>2.528/4.424</td>
<td>0.968</td>
</tr>
<tr>
<td><strong>Fe/FeF$_3$</strong></td>
<td>0/3</td>
<td>0.000/2.105</td>
<td>0.968</td>
</tr>
<tr>
<td><strong>FeS/FeF$_3$</strong></td>
<td>2/3</td>
<td>0.230/2.105</td>
<td>0.971</td>
</tr>
<tr>
<td><strong>FeCl$_2$ · 4H$_2$O/FeF$_3$</strong></td>
<td>2/3</td>
<td>0.604/2.105</td>
<td>0.978</td>
</tr>
<tr>
<td><strong>FeSO$_4$/FeF$_3$</strong></td>
<td>2/3</td>
<td>0.442/2.105</td>
<td>0.974</td>
</tr>
<tr>
<td><strong>FeCl$_2$ · 4H$_2$O/FeSO$_4$</strong></td>
<td>2/2</td>
<td>0.604/0.442</td>
<td>1.003</td>
</tr>
<tr>
<td><strong>Fe(NO$_3$)$_3$ · 9H$_2$O/FeF$_3$</strong></td>
<td>3/3</td>
<td>0.181/2.105</td>
<td>0.970</td>
</tr>
<tr>
<td><strong>FeCl$_3$ · 6H$_2$O/FeF$_3$</strong></td>
<td>3/3</td>
<td>0.906/2.105</td>
<td>0.982</td>
</tr>
<tr>
<td><strong>Fe$_2$O$_3$/FeF$_3$</strong></td>
<td>3/3</td>
<td>1.543/2.105</td>
<td>0.992</td>
</tr>
<tr>
<td><strong>Co/CoF$_3$</strong></td>
<td>0/3</td>
<td>0.000/2.105</td>
<td>0.973</td>
</tr>
<tr>
<td><strong>Co(ClO$_4$)$_2$ · 6H$_2$O/CoF$_3$</strong></td>
<td>2/3</td>
<td>0.121/2.105</td>
<td>0.974</td>
</tr>
<tr>
<td><strong>Co(ClO$_4$)$_2$ · 6H$_2$O/CoCl$_2$ · 6H$_2$O</strong></td>
<td>2/2</td>
<td>0.121/0.604</td>
<td>0.994</td>
</tr>
<tr>
<td><strong>Co(NO$_3$)$_2$ · 6H$_2$O/CoF$_3$</strong></td>
<td>2/3</td>
<td>0.121/2.105</td>
<td>0.974</td>
</tr>
<tr>
<td><strong>CoCl$_2$ · 6H$_2$O/CoF$_3$</strong></td>
<td>2/3</td>
<td>0.604/2.105</td>
<td>0.980</td>
</tr>
<tr>
<td><strong>CoO/CoF$_3$</strong></td>
<td>2/3</td>
<td>1.028/2.105</td>
<td>0.986</td>
</tr>
<tr>
<td><strong>CoF$_2$/CoF$_3$</strong></td>
<td>2/3</td>
<td>0.018/2.105</td>
<td>0.991</td>
</tr>
<tr>
<td><strong>Ni/NiSO$_4$</strong></td>
<td>0/2</td>
<td>0.000/0.442</td>
<td>0.995</td>
</tr>
<tr>
<td><strong>Ni/NiCl$_2$</strong></td>
<td>0/2</td>
<td>0.000/0.604</td>
<td>0.993</td>
</tr>
<tr>
<td><strong>NiSO$_4$/NiCl$_2$</strong></td>
<td>2/2</td>
<td>0.442/0.604</td>
<td>0.998</td>
</tr>
<tr>
<td><strong>Cu/Cu(NO$_3$)$_2$ · 3H$_2$O</strong></td>
<td>0/2</td>
<td>0.000/0.121</td>
<td>0.998</td>
</tr>
<tr>
<td><strong>Cu(CN)/Cu(NO$_3$)$_2$ · 3H$_2$O</strong></td>
<td>1/2</td>
<td>0.060/0.121</td>
<td>0.999</td>
</tr>
<tr>
<td><strong>CuI/Cu(NO$_3$)$_2$ · 3H$_2$O</strong></td>
<td>1/2</td>
<td>0.086/0.121</td>
<td>0.999</td>
</tr>
<tr>
<td><strong>Cu(C$_2$O$_4$)/Cu(NO$_3$)$_2$ · 3H$_2$O</strong></td>
<td>2/2</td>
<td>0.442/0.121</td>
<td>1.002</td>
</tr>
<tr>
<td><strong>CuBr$_2$/Cu(NO$_3$)$_2$ · 3H$_2$O</strong></td>
<td>2/2</td>
<td>0.366/0.121</td>
<td>1.002</td>
</tr>
<tr>
<td><strong>CuCN/CuI</strong></td>
<td>1/1</td>
<td>0.060/0.086</td>
<td>0.999</td>
</tr>
<tr>
<td><strong>Cu(C$_2$O$_4$)/CuI</strong></td>
<td>2/1</td>
<td>0.442/0.086</td>
<td>1.003</td>
</tr>
<tr>
<td><strong>CuBr$_2$/CuI</strong></td>
<td>2/1</td>
<td>0.366/0.086</td>
<td>1.003</td>
</tr>
<tr>
<td><strong>Zn/ZnSO$_4$</strong></td>
<td>0/2</td>
<td>0.000/0.442</td>
<td>0.996</td>
</tr>
<tr>
<td><strong>Zn/ZnCl$_2$</strong></td>
<td>0/2</td>
<td>0.000/0.774</td>
<td>0.993</td>
</tr>
<tr>
<td><strong>ZnSO$_4$/ZnCl$_2$</strong></td>
<td>2/2</td>
<td>0.442/0.774</td>
<td>0.997</td>
</tr>
</tbody>
</table>
3. Experimental

The samples are excited by 59.5 keV γ rays from a filtered $^{241}$Am radioactive source and X-rays emitted from samples were detected by a Ge(Li) (FWHM = 190 eV at 5.9 keV) and Si(Li) (FWHM = 160 eV at 5.9 keV) detectors coupled to a ND66B multichannel analyser. Two typical spectra of ZnSO$_4$ and ZnCl$_2$ are given in Fig. 1 and Fig. 2. Ni and Zn foil samples were corrected as regards to self-absorption while other samples were subjected to particle size correction since they were in powdered form and the samples were very thin. Powder samples were prepared by using the sample preparation cylindrical cup and rod produced in our research laboratory and supported on the mylar film $50 \times 10^{-4}$ g • cm$^{-2}$ thickness and 3.4 cm diameter. Detector efficiency corrections were carried on data. The efficiency calibration of the system was made by using reference lines of the known intensity in $^{241}$Am, $^{57}$Co, $^{137}$Cs, and $^{54}$Mn standard sources under the same experimental geometric conditions. Therefore the absorption effects of the mylar film and the air in the path of the photons were also eliminated. The background was measured by using the calculation of the mean from ten channels.

Fig. 1. A typical spectrum of ZnSO$_4$. 
A. Kücükönder et al.

Fig. 2. A typical spectrum of ZnCl$_2$.

except the region about the joining of the $K\alpha$ and $K\beta$ peaks. Sample preparation, experimental method and various correction applied to data have been described more detailed in previous papers [17–21].

4. Results and discussion

The results for the $K\beta/K\alpha$ intensity ratio are presented together with previously published theoretical and experimental results in Table II. Our calculated results are in good compliance with literature data [9, 23]. Our experimental values for Mn compounds (MnCl$_2$·4H$_2$O)/KMnO$_4$ and (MnCl$_2$·4H$_2$O)/[Mn(NO$_3$)$_2$·H$_2$O] are in agreement with calculations. Table II also shows that the calculated $K\beta/K\alpha$ ratios in other manganese compounds agree with earlier experimental studies [8, 9, 17–19] within 4%. The calculated Mn/(KMnO$_4$) ratio differs from our previous experimental value by $\approx 7\%$. For Fe compounds and (FeCl$_2$·4H$_2$O)/(FeF$_3$) ratio, it can be seen that the agreement between calculations and experiment is within 3%. Calculated $K\beta/K\alpha$ intensity ratio for the other compounds of Fe are in agreement with our earlier experimental results [19] within 4%. $K\beta/K\alpha$ ratios calculated for Co compounds agree with present and
our previous experimental results [17] within 12%. From Table II it can be seen that the agreement between calculated values and experiment for Ni is very good and lies within 1%. The experimental $K_\beta/K_\alpha$ ratios for Cu compounds differ up to 4% and in these compounds difference between calculated value and experimental results lies within 4%. Table II shows that calculated $K_\beta/K_\alpha$ ratio values of Zn also agree with experimental results. Differences between values of Zn are insignificant. The reason of this may be that the 3d shell of Zn is fully occupied and chemical effects are not expected to change relative $K_\beta/K_\alpha$ intensity ratios of Zn compounds. The insignificant difference between calculations and experiment can be attributed to experimental uncertainties and errors.

The relative $K_\beta/K_\alpha$ ratios depended on the type of chemical bond, the polarity of the complex or crystal, the coordination number, the ionic character of the chemical bond, and the ligands attached to the emitting atom. In addition, it is clearly evident from the calculated and experimental data that the relative $K_\beta/K_\alpha$ X-ray intensity ratios vary in accordance to the valence charge difference. This variation depends on the difference of the electronegativities of the bonding atoms and the oxidation number of the related metal atom. It is generally observed that as the ratio of the oxidation number of the related metal atom in one compound to the oxidation number of the related metal atom in another compound (oxidation number)$_1$/(oxidation number)$_2$ is increased, the relative $K_\beta/K_\alpha$ X-ray intensity ratios increase as well.

References