Valence Sensitivity of EELS White-Line Extraction Methods

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Electron energy-loss (EEL) white-lines of transition metals contain rich information on the crystallographic site and the charge state of the excited element [1,2]. In this way, the Mn-L_{2,3} lines show characteristic changes with Mn valency, among those the ratio of the L_3- to the L_2-intensity [3,4].

To determine the white-line intensities from experimental EEL spectra four different approaches have been analyzed with focus on their Mn valence sensitivity in the range [Mn^{3+}; Mn^{4+}]. We found that the maximum-intensity as well as Pearson’s [5] and Walsh-Dray [6] methods yield noticeably larger relative ratio changes than curve-fitting (Table 1). As a measure for the Mn valency distinction power the ratio change related to the scattering was evaluated for the curve-fitting and Walsh-Dray methods. According to this measure Walsh-Dray distinguishes more strongly between Mn^{3+} and Mn^{4+} (Table 1) and represents therefore the preferred method to analyze the Mn valency in mixed-valency manganites.

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Table 1. Change of \( I(L_3) / I(L_2) \) and valence sensitivities (last row) for the analyzed extraction methods; all data refer to a representative spectrum set.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Method</th>
<th>Maximum-Intensity</th>
<th>Pearson</th>
<th>Curve-fitting</th>
<th>Walsh-Dray</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\Delta[I(L_3)/I(L_2)]_{Mn^{3+};Mn^{4+}}]</td>
<td>Absolute change</td>
<td>0,31</td>
<td>0,35</td>
<td>0,24</td>
<td>0,38</td>
</tr>
<tr>
<td>[\Delta[I(L_3)/I(L_2)]<em>{Mn^{3+};Mn^{4+}}/mean[I(L_3)/I(L_2)]</em>{Mn^{3+};Mn^{4+}}]</td>
<td>Relative change</td>
<td>18 %</td>
<td>15 %</td>
<td>9 %</td>
<td>16 %</td>
</tr>
<tr>
<td>[\Delta[I(L_3)/I(L_2)]<em>{Mn^{3+};Mn^{4+}}/stddev[I(L_3)/I(L_2)]</em>{Mn^{3+};Mn^{4+}}]</td>
<td>(*)</td>
<td>(*)</td>
<td>1,4</td>
<td>3,5</td>
<td></td>
</tr>
</tbody>
</table>

* excluded from comparison due to presence of continuum (Maximum-Intensity) or large statistical errors (Pearson)

References

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