FUNDAMENTAL PARAMETER METHOD FOR THE LOW ENERGY REGION INCLUDING CASCADE EFFECT AND PHOTOELECTRON EXCITATION

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ABSTRACT

We have demonstrated the cascade effect and the secondary photoelectron excitation effect by means of Cr-L line measurements by using monochromatic radiation of high spectral purity and well-known flux provided by two beamlines of the Physikalisch-Technische Bundesanstalt (PTB), Germany’s national institute of metrology at the electron storage ring BESSY II. The plane grating monochromator beamline for undulator radiation covers the energy range from 30 eV to 1.9 keV, and the four-crystal monochromator beamline for synchrotron radiation from 1.75 keV to 10.5 keV. The Cr-L fluorescence intensities show a considerable jump at Cr-K edge energy as the source photon energy rises, indicating the magnitude of the cascade effect. The fundamental parameter method including the cascade effect and the secondary photoelectron excitation effect shows good agreement with the measurement. The evaluation of this computation method for the measurement carried out with a conventional XRF spectrometer also shows good performance of the calculation.

INTRODUCTION

Low-energy characteristic X-ray measurements play a key role in X-ray fluorescence (XRF) analysis of light elements and of thin layer materials. Besides primary excitation by incident X-rays and secondary excitation by fluorescent X-rays, there are other secondary processes which contribute to low-energy characteristic X-ray emissions. One of them is the excitation by photoelectrons, which has been introduced into a fundamental parameter method¹ and evaluated experimentally². Another process is the emission of L-series X-rays following radiative and non-radiative relaxations of the K-shell ionization.

This “cascade” effect on L-series X-ray emission occurs when the energy of source X-rays is higher than the K-shell binding energy, i.e. in a measurement of L-lines of low energy using an XRF spectrometer with, for example, a Rh-target end-window tube. The contribution of the cascade effect exceeds that of direct excitation in these situations. Obviously, this effect can contribute also to M-series X-ray emission. Although this cascade effect was studied already³, neither a recent implementation in a fundamental parameter software nor experimental evaluation have been reported. The extension of XRF application, however, requires measurements of L- or M-lines, in which the cascade effect arises.
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In this paper, we demonstrate the implementation of the cascade effect into the fluorescent intensity calculation as well as its experimental evaluation using monochromatic radiation provided by two PTB beamlines and a conventional XRF spectrometer.

**CALCULATION**

The implementation formula used for the cascade effect term is shown in Figure 1. Here, the values given by Rao et al.\(^4\) for the total number of holes in an L-subshell after relaxation of K-shell have been used.

\[
I_{iqs}^{\text{Cascade}} = \int_{\lambda} \int_{z} d\lambda I_{0}(\lambda) \exp\left(-\rho \frac{\mu(\lambda)}{\sin \psi_{in}} + \frac{\mu(\lambda_{iqs})}{\sin \psi_{out}}\right) \omega_{iq} R_{iq}^{s}
\]

\[\lambda: \text{Incident X-ray wavelength}\]
\[I_{0}(\lambda)d\lambda: \text{Intensity of incident X-rays}\]
\[\mu(\lambda): \text{Mass absorption coefficient of the specimen for X-rays of wavelength } \lambda\]
\[\lambda_{iqs}: \text{Wavelength of } iqs \text{ line}\]
\[\rho: \text{Specimen density}\]
\[w_{i}: \text{Mass fraction of element } i \text{ in the specimen}\]
\[\tau(\lambda): \text{Photo-absorption coefficient of element } i \text{ for X-rays of wavelength } \lambda\]
\[K_{ip}: \text{Fraction of shell } p \text{ in photo-absorption coefficient; } K_{ip} = (1 - 1/j_{ip}) / \Pi j_{i}\]
\[j_{ip}: \text{Jump ratio at edge } p \text{ of element } i\]
\[\lambda_{ip}: \text{Wavelength at edge } p \text{ of element } i\]
\[\omega_{iq}: \text{Fluorescent yield of shell } q \text{ of element } i\]
\[R_{iq}^{s}: \text{Relative transition probability of } iqs \text{ line in } iq \text{ series}\]
\[\Psi_{in}: \text{Incident angle}\]
\[\Psi_{out}: \text{Take-off angle}\]
\[n_{ip->q}: \text{Total number of holes in } q \text{ shell generated after relaxation of a hole in } p \text{ shell}\]

**EXPERIMENTS**

Two experiments were performed to evaluate the calculation. One of them, using tunable radiation, was carried out in the radiometry laboratory of PTB at the third generation 1.7 GeV electron storage ring BESSY II in Berlin\(^5\). Beside other beamlines intended for radiometric tasks, a plane-grating monochromator (PGM) beamline for undulator radiation and a four-crystal monochromator (FCM) beamline for bending magnet radiation provide monochromatized radiation of high spectral purity. The photon energies available at the PGM range from 30 eV to 1.9 keV and at the FCM from 1.75 keV to 10 keV. Within the present investigation, requiring photon energies between 300 eV and 8000 eV, the 1200 l/mm Au coated grating at the PGM and the Si(111) crystals at the FCM were employed. At a given photon energy of interest, the radiant power of the incident excitation radiation was adapted to the count-rate capability of the Si(Li) detector used by either varying the trigonometric ratio of the angle of incidence to the angle of...
diffraction at the PGM or by detuning the second pair of Si crystals at the FCM. The set of experiments was carried out in the ultra-high vacuum XRF irradiation chamber of PTB placed in the focal plane of the PGM and of the FCM beamlines. This chamber allows simultaneous handling and accurate positioning of six samples with an effective diameter of 10 mm that are oriented vertically. The angle at which the exciting radiation is incident on the sample of interest can be varied between 30° and 90°. In this work, both angles of incidence and take-off were set to 45°. The scattered and fluorescence radiation were registered by an energy-dispersive Si(Li) detector with a 0.2 µm thick Si window placed behind an calibrated aperture, which is 67 mm away from the sample center. In addition, the efficiency of such a detector was determined in absolute terms with a relative uncertainty ranging from 1.5 % to 2 % at the photon energies of interest. The schematic configuration is shown in figure 2. The specimen used for this experiment was a 2 µm thick chromium layer deposited on a silicon wafer. The spectral region of interest was that of Cr-L fluorescent radiation.

The other experiment was performed using a sequential fluorescent X-ray spectrometer Rigaku ZSX 100e equipped with a Rh end-window tube, the window thickness being 30 µm. The measurements were carried out in two excitation conditions of 30 kV with no primary filter, and 50 kV with a 25 µm thick aluminum filter to see the contribution of the cascade effect. The specimens for these measurements were a nickel metal, steel and Ni-alloy standard samples from Brammer and a film standard sample from Micromatter. The compositions of these specimens are listed in table 1. The measured fluorescence line was Ni-Lα.

### Table 1. List of the specimens used in the experiment with the spectrometer with their standard content values (trace elements have been omitted).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Deposition mass (µg/cm²)</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Ti</th>
<th>Cu</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni metal</td>
<td>100</td>
<td>100</td>
<td>41.34</td>
<td>0.87</td>
<td>22.20</td>
<td>0.46</td>
<td>0.26</td>
<td>0.30</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BNRM5179</td>
<td>34.1</td>
<td>43.1</td>
<td>0.065</td>
<td>28.65</td>
<td>0.36</td>
<td>21.85</td>
<td>0.71</td>
<td>1.92</td>
<td>2.82</td>
<td>0.08</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>BNRM825</td>
<td>53.7</td>
<td>10.59</td>
<td>1.47</td>
<td>0.02</td>
<td>19.17</td>
<td>3.19</td>
<td>0.0026</td>
<td>9.96</td>
<td>0.13</td>
<td>1.50</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>BNRM198</td>
<td>56.9</td>
<td>13.53</td>
<td>1.27</td>
<td>0030</td>
<td>19.28</td>
<td>3.04</td>
<td>0.022</td>
<td>4.17</td>
<td>0.06</td>
<td>1.38</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>BNRM199</td>
<td>23.6</td>
<td>1.63</td>
<td>0.92</td>
<td>22.27</td>
<td>0.02</td>
<td>0.36</td>
<td>13.91</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel on mylar film</td>
<td>43.7</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### RESULT AND DISCUSSION

Figure 3 presents the comparison between measured and calculated Cr-L fluorescent intensities. The experimental results obtained by use of monochromatic radiation and three types of calculated results are shown. The three calculations cover (i) the result obtained by primary and secondary fluorescent X-rays only, (ii) by primary and secondary fluorescent X-rays and
secondary photoelectron excitation, (iii) the result consisting of primary and secondary fluorescent X-rays, secondary photoelectron excitation and the cascade effect. This figure shows Cr-L intensities in log scale against incident photon energy. The experimental data show a drastic jump at the Cr-K edge energy. This jump illustrates the cascade effect very well. Calculations (i) and (ii) show no jump at the Cr-K edge, although calculation (ii) is in line with the experiment below the edge, illustrating the contribution of the secondary photoelectron excitation. In contrast to this, the calculation (iii) reproduces the jump at the Cr-K edge. Part of the remaining difference between the measured data and the calculation above the Cr-K edge would be due to the Coster-Kronig transition, which still must be included into the calculation.

Figure 3. Experimental and calculated results for Cr-L fluorescence intensities from the 2 µm thick chromium layer deposited on a silicon wafer using monochromatized radiation at the PTB lab at BESSY II. Dots: experimental results. Dotted line: the calculated results obtained by primary and secondary fluorescent X-rays only. Dashed line: the calculated results, which consist of primary and secondary fluorescent X-rays and the secondary photoelectron excitation. Solid line: the results obtained by calculation, which includes primary and secondary fluorescent X-rays, secondary photoelectron excitation and the cascade effect.

Figure 4 presents the comparison between measured and calculated intensities of Ni-Lα. The experimental results obtained by use of the spectrometer with the excitation voltage of 30 kV compared with two types of calculation results are shown. Graphs (a) and (b) are identical data sets, but data values in (b) have been normalized by the Ni-Lα intensity for the nickel metal specimen. These two calculations are (i) the result obtained by primary and secondary fluorescent X-rays only, (ii) the results, which include primary and secondary fluorescent X-rays, secondary photoelectron excitation and the cascade effect. The difference between (i) and (ii) is very small, meaning that the contribution of the cascade and photoelectron excitation effects to
Ni-L_α emission is only slight in this excitation condition. This is due to the tube spectrum. In this excitation condition using a tube equipped with an ultra-thin-window, Rh-L lines, which cannot contribute to the cascade effect, are very intense in comparison with the Rh-K lines (see table 2).

![Graph](a)

**Excitation voltage: 30kV, primary filter: none**

- Calculated intensity vs. Measured intensity
- Normalized calculated intensity vs. Normalized measured intensity

Figure 4. Experimental and calculated results for Ni-L_α fluorescence intensities from the 7 different specimens listed in table 1, using a sequential spectrometer equipped with a Rh end-window tube, with a 30 µm thick Be window. The measurements were carried out under the excitation conditions of 30 kV without any primary filter. Squares: the calculation results obtained by primary and secondary fluorescent X-rays only. Circles: the results obtained by calculation, which covers primary and secondary fluorescent X-rays, secondary photoelectron excitation and the cascade effect.

Table 2. Characteristic X-ray intensities from a Rh end-window tube with a 30 µm thick Be window in two conditions. [A]: excitation voltage: 30 kV, Primary filter: none; [B]: excitation voltage: 50 kV, primary filter: 25 µm thick Al.

<table>
<thead>
<tr>
<th>Line name</th>
<th>Rh-K_α</th>
<th>Rh-K_β</th>
<th>Rh-L_α</th>
<th>Rh-L_β1</th>
<th>Rh-L_β2</th>
<th>Rh-L_β3</th>
<th>Rh-L_γ1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength[A]</td>
<td>0.61470</td>
<td>0.54559</td>
<td>4.5982</td>
<td>4.3741</td>
<td>4.1310</td>
<td>4.2665</td>
<td>3.9437</td>
</tr>
<tr>
<td>Intensity</td>
<td>Condition[A]</td>
<td>900.05</td>
<td>185.82</td>
<td>20309</td>
<td>9676.9</td>
<td>1142.2</td>
<td>1891.2</td>
</tr>
</tbody>
</table>

To enhance the cascade effect and to evaluate the calculation, we performed another measurement with an excitation voltage of 50 kV using a 25 µm thick aluminum primary filter. The result is shown in figure 5 in the same manner as figure 4. Figure 5(a) illustrates that the contribution of the cascade effect is large in the calculation due to the enhanced Rh-K lines and suppressed Rh-L lines. Furthermore, in figure 5(b), the normalized intensity plot, the new calculation gives all data points on a single line not only for bulk samples but also for the thin
film specimen. However, when using the conventional calculation, the data point of the thin film specimen does not lie on the line connecting the data points of bulk samples.

![Graph](image)

**Figure 5.** Experimental and calculated results for Ni-L\(\alpha\) fluorescence intensities from the specimens listed in table 1 using a sequential spectrometer equipped with a Rh end-window tube having a 30 µm thick Be window. The measurements were carried out with the excitation conditions of 50 kV with a 25 µm thick aluminum filter. Squares: the calculation results obtained by primary and secondary fluorescent X-rays only. Circles: the results obtained by the calculation, which covers primary and secondary fluorescent X-rays, secondary photoelectron excitation and the cascade effect.

**CONCLUSION**

The implementation of the cascade effect into the intensity calculation has been described. The cascade effect as well as the secondary photoelectron excitation effect was observed in two different experimental situations. The calculation was validated by experiments using both monochromatized radiation and a WDXRF spectrometer. In the experiment using the WDXRF spectrometer with an ultra-thin window tube in usual excitation condition, the contribution of the cascade effect was only slight.

**REFERENCES**