Model based quantification of EELS spectra: including the fine structure

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Abstract

An extension to model based electron energy loss spectroscopy (EELS) quantification is reported to improve the possibility of modelling fine structure changes in electron energy loss spectra. An equalisation function is used in the energy loss near edge structure (ELNES) region to model the differences between a single atom differential cross section and the cross section for an atom in a crystal. The equalisation function can be shown to approximate the relative density of unoccupied states for the given excitation edge. On a set of 200 experimental h-BN spectra, this technique leads to statistically acceptable models resulting into unbiased estimates of relative concentrations and making the estimated precisions come very close to the Cramér-Rao lower bound (CRLB). The method greatly expands the useability of model based EELS quantification to spectra with pronounced fine structure. Another benefit of this model is that one also gets an estimate of the unoccupied density of states for a given excitation edge, without having to do background removal and deconvolution, making the outcome intrinsically more reliable and less noisy.

\textit{Key words:} EELS; Fitting; Quantification; Precision; Maximum likelihood; Model

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1 Introduction

Building on the framework as described in [1] we propose a new model to better describe excitation edges with pronounced fine structure features. The fine structure of an EELS excitation edge is generated by solid state effects that alter the density of unoccupied states. For determining elemental concentrations from EELS spectra one is in principle not interested in these fine structures.
structures but they hinder the quantification because the edges will deviate from a simple single atomic cross section spectrum. This problem does not occur in energy dispersive X-ray spectroscopy (EDX) due to the much worse energy resolution (≈ 100 eV) which blurs out the fine structure details.

The probability for inelastic scattering in a solid angle Ω and with an energy loss between $E_i$ and $E_{i+1}$ is given by [2]:

$$J(E_i) = \int_{E_i}^{E_{i+1}} M(E)N(E)dE$$  \hspace{1cm} (1)

With $E$ the energy loss, $Ω$ the solid angle into which scattering occurs and $N(E)$ the density of states (DOS) function determining whether a certain final state $|f\rangle$ with excitation energy $E$ is occupied or not. The matrix element $M(E)$ is given by:

$$M(E) = \int_{Ω} \frac{d^2\sigma}{dΩdE}dΩ \propto \int_{Ω} \frac{1}{q^2E} df dΩ$$  \hspace{1cm} (2)

with:

$$f(E, q) = \sum_{|f\rangle} \frac{E}{q^2} |\langle i| \sum_j^N e^{iqr_j}|f\rangle|^2 \delta(E_i - E_f - E)$$  \hspace{1cm} (3)

where $\frac{d^2\sigma}{dΩdE}$ is the double differential cross section and $f$ is the generalised oscillator strength (GOS) for exciting an initial N-particle state $|i\rangle$ to all final states $|f\rangle$ with energy $E_f$, momentum transfer $q$ and position coordinates of the atomic electrons $r_j$. For a single atom this becomes:

$$J_{\text{free}}(E_i) = \int_{E_i}^{E_{i+1}} M_{\text{free}}(E)N_{\text{free}}(E)dE$$  \hspace{1cm} (4)

A cross section for an atom in a crystal, on the other hand, must be written as:

$$J_{\text{cryst}}(E) = \int_{E_i}^{E_{i+1}} M_{\text{cryst}}(E)N_{\text{cryst}}(E)dE$$  \hspace{1cm} (5)

In general, both matrix elements, $M_{\text{free}}(E)$ and $M_{\text{cryst}}(E)$, will be different, especially because the final states in a crystal will differ from the final states in
a single atom. Moreover the matrix element will be dependent on the crystal orientation via the momentum transfer $q$ [3]. If we assume however that both $M(E)$ are approximately the same for materials with weak anisotropy we can write $M_{\text{cryst}}(E) \approx M_{\text{free}}(E)$. This enables us to write:

$$J_{\text{cryst}}(E_i) = \int_{E_i}^{E_{i+1}} M_{\text{cryst}}(E) N_{\text{free}}(E) \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)} dE$$

(6)

$$J_{\text{cryst}}(E_i) \approx \int_{E_i}^{E_{i+1}} M_{\text{free}}(E) N_{\text{free}}(E) \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)} dE$$

(7)

$$J_{\text{cryst}}(E_i) \approx J_{\text{free}}(E_i) D(E_i)$$

(8)

assuming that $N(E)$ is constant in the range $E_i$ till $E_{i+1}$ with

$$D(E) = \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)}$$

(9)

$D(E)$ is a function that equalises the shape of the free atom cross section to model the real shape of the excitation edge. $D(E)$ is approximately equal to the unoccupied DOS relative to the DOS of a free atom if the following assumptions hold:

- The matrix element $M(E)$ is isotropic.
- The excitations come from a single core state with a well defined energy: otherwise $D(E)$ is a convoluted relative DOS like e.g. in an $L_{2,3}$ edge with spin split 2p core states.

Note that as usual the cross section $J(E)$ is only sensitive to the angular momentum projected DOS because in the dipole approximation only matrix elements that obey the $\Delta l = \pm 1$ rule are non-zero. With $\Delta l$ the change in angular momentum between initial and final state, $|i\rangle$ and $|f\rangle$.

In cases where these assumptions do not hold, we can still formally use Eq. 8, but $D(E)$ merely becomes an equalisation function without a direct physical interpretation in terms of the DOS.

One can model $D(E)$ by a piecewise linear function with $n$ data points $D_j(E_j)$ which is zero for $E < E_{\text{start}}$ and is one for $E > E_{\text{stop}}$ as in fig. 1. In this way, one obtains a model for the excitation edge with $n$ extra parameters. The fact that $D(E)$ goes to one is based on the assumption that excitations to the continuum ($E > E_{\text{stop}}$) are independent on the details of the atom environment and are mainly determined by the energy of the core state with respect to the ionisation level as sketched in fig. 2.
In practice $E_{\text{start}}$ will be chosen just below the edge onset while $E_{\text{stop}}$ is chosen approximately as the ionisation energy or alternatively as the energy from which there is no longer a significant fine structure modulation in the spectrum.

Inclusion of multiple scattering by convolution with the low loss spectrum \[1\] will smooth the edge containing the fine structure equalisation. This is due to the fact that the experimental low loss spectrum itself can be seen as a convolution of the true low loss spectrum with the energy distribution of the gun and the energy resolution function of the spectrometer which leads to smoothing if a reasonable sampling of the spectrum is chosen. Because of this smoothing, it is advisable to choose the number of data points $n$ in the fine structure model $D(E)$ so that the energy interval between the tabulated points is of the order of the energy resolution of the spectrometer. Taking more closely spaced intervals will not affect the smoothed model significantly and may have the unfavorable effect of deteriorating the precision of the parameter estimates. Moreover it leads to a noisy estimate of $D(E)$ and is similar to trying to deconvolute a spectrum to reveal information beyond the energy resolution of the spectrometer.

Making an appropriate choice for $E_{\text{start}}$, $E_{\text{stop}}$ and $n$, the user creates a model which is now capable of fitting spectra with fine structure details much closer than what is possible with simple single atom cross sections. The downside is the increase of the number of model parameters which may deteriorate the precision of the parameter estimates. However, it will be shown that this is only a minor effect since the parameters are weakly correlated. The positive side is the fact that the model is now more likely to be statistically accepted using model validation as presented in \[1\]. Another advantage is that one also gets an estimate of the $D(E)$ function which can be seen as an estimate of the density of unoccupied states, under the assumptions given above. Note that the estimated $D(E)$ is immediately a single scattering $D(E)$ as opposed to the conventional way of obtaining fine structure information where one has to do background removal as well as a multiple scattering deconvolution process \[2\].

2 Experiment

A powder of h-BN \[4,5\] (Sigma Aldrich) was heated at 500°C for 4h to remove contamination problems. Successively the powder was crushed in ethanol and dispersed on a holey carbon TEM grid. A Jeol 3000F TEM with field emission gun and a Gatan GIF2000 spectrometer were used to record EELS spectra at a collection angle of 2.55 mrad and negligible convergence angle ($< 0.2$ mrad). A total of 200 EELS spectra were recorded from the same area of the sample to obtain replications of the same experiment.
Fig. 1. Schematic drawing of the $D(E)$ function.

Fig. 2. Schematic drawing of the difference in states between a free atom and an atom in a crystal, showing that they are mainly different in the ELNES region close to the ionisation energy but very similar for excitation to the continuum band.
The spectrum is modelled using a power law background and two Hartree-Slater edges [6] for the B and N K-edge. Two different models are compared:

- Model A: without fine structure modelling
- Model B: with fine structure modelling (20 points from 399 eV till 450 eV for the N K-edge and 55 points from 191 eV till 260 eV for the B K-edge)

Note the lower sampling for the N K-edge as a consequence of the higher lifetime broadening in this peak as compared to the B K-edge. Furthermore we assume that the observations, that is, the measured intensity values of the spectrum, are independent Poisson distributed.

The parameters of model A and B are estimated using the maximum likelihood (ML) estimator [1]. The reason for choosing the ML estimator is that it has some favorable statistical properties [7]. First it can be shown that the estimator asymptotically achieves the so-called Cramér-Rao lower bound (CRLB), which is a lower bound on the variance of any unbiased estimator of the parameters [7,10]. Asymptotically means for an infinite number of observations, in this paper, energy points in the spectrum. Therefore the ML estimator is asymptotically most precise. Secondly, it can be shown that the ML estimator is consistent, which means that it converges to the true value of the parameter in a statistically well defined way if the number of observations increases. Thirdly, the ML estimator is asymptotically normally distributed with a mean equal to the true value of the parameter and a variance-covariance matrix equal to the CRLB. Whether these asymptotic properties also apply to a finite or even small number of observations can often only be assessed by estimating from artificial, simulated observations. In [1] it has been shown that the number of observations of one spectrum is usually large enough for these asymptotic properties to be valid.

Fig. 3 shows one spectrum out of a series of 200 together with model A evaluated at the corresponding ML estimates. In fig. 4, this is done for model B. Next, from the obtained ML estimates an estimate of the ratio B/N has been obtained for each spectrum using the so-called invariance property of the ML estimator [8]. Furthermore, for each experimental spectrum, the CRLB has been estimated by substituting the ML estimates in the expression for the CRLB following the procedure as discussed in [1,7,9]. In this way, one may obtain a measure for the precision of the B/N ratio provided that the model is valid. The distribution of the estimated B/N ratio is shown in fig. 5 and fig. 6 for situation A and B, respectively, together with a normal distribution with mean and variance equal to the estimated mean of the 200 ML estimated B/N ratios and the mean of the corresponding 200 estimated CRLB’s, respectively.

Table 1 presents an overview of the results obtained for the two models used. The first three rows show the 95% confidence intervals for the mean of the
Fig. 3. Model A evaluated at the ML estimates (full line) and the corresponding experimental spectrum (points) from the set of 200 spectra, showing the poor fit between experiment and model due to the pronounced fine structure which is not included in model A.

Fig. 4. Model B evaluated at the ML estimates (full line) and the corresponding experimental spectrum (points) from the set of 200 spectra, showing the good fit between experiment and model when including the fine structure making it difficult to distinguish between them.

200 estimated ratios of B/N, the standard deviation of these estimates and the mean of the estimated lower bounds on the standard deviation, that is, the square root of the estimated CRLB’s. The last three rows show the results obtained from the likelihood ratio test [7]. This is a statistical hypothesis test which is appropriate for model validation. More specifically, these rows show the percentage of accepted models for different values of the significance level $\alpha$, or equivalently, the test size. The meaning of this significance level $\alpha$ is that if the model is valid, the probability of accepting this model is $1 - \alpha$. 

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Fig. 5. Distribution of the estimated B/N ratio from 200 spectra (bars) using model A together with the normal distribution with mean and variance equal to the estimated mean of the 200 ML estimated B/N ratios and mean of the corresponding 200 estimated CRLB’s, respectively. Note the discrepancy between both distributions in case no fine structure is included.

Fig. 6. Distribution of the estimated B/N ratio from 200 spectra (bars) using model B together with the normal distribution with mean and variance equal to the estimated mean of the 200 ML estimated B/N ratios and mean of the corresponding 200 estimated CRLB’s, respectively. Note the reasonably good fit between both distributions.

3 Discussion

From table 1 it is clear that model A is rejected by the likelihood ratio test for model validation [1] while model B is accepted. This clearly shows that extending EELSMODEL [11] with a way to model the fine structure greatly improves the useability for spectra with pronounced fine structure features like for h-BN. Since the model is accepted, one can trust the parameter estimates and the corresponding estimates of the precision using the CRLB. Indeed, the experimental distribution for the B/N ratio using model B is reasonably well
Table 1
Summary of the results for model A and B.

<table>
<thead>
<tr>
<th></th>
<th>model A (no fine structure)</th>
<th>model B (fine structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean B/N ratio</td>
<td>(1.0702, 1.0720)</td>
<td>(1.0447, 1.0473)</td>
</tr>
<tr>
<td>standard deviation</td>
<td>(0.0071, 0.0086)</td>
<td>(0.0101, 0.0123)</td>
</tr>
<tr>
<td>estimated precision using CRLB</td>
<td>(0.00416, 0.00417)</td>
<td>(0.00844, 0.00847)</td>
</tr>
<tr>
<td>accepted at $\alpha = 0.05$</td>
<td>0</td>
<td>91%</td>
</tr>
<tr>
<td>accepted at $\alpha = 0.25$</td>
<td>0</td>
<td>76%</td>
</tr>
<tr>
<td>accepted at $\alpha = 0.5$</td>
<td>0</td>
<td>60%</td>
</tr>
</tbody>
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The obtained standard deviation from model B remains higher than the lower bound by an amount that can not be explained by the finite amount of replications as can be seen from the non-overlapping confidence intervals between the estimated precision using CRLB and the sample standard deviation. The reason why the CRLB is only approached could be due to the simplistic uncorrelated Poisson noise model. In reality correlation exists in the recording process, but further research is needed on how to include it in a model based fitting process. On top of that we note that a bias exists for model A as the mean B/N ratio is significantly different from model B.

4 Conclusion

It was demonstrated that it is possible to create useful models for spectra with a pronounced fine structure by applying an equalisation function with a number of extra parameters. The equalisation function was shown to approximate the relative density of unoccupied states for the given excitation edge. The importance of including the fine structure in the model was demonstrated on a set of spectra from h-BN. The experiment showed that with a modest number of extra parameters a statistically acceptable model could be created which is of primary importance if we are to trust the estimated parameters and the precision estimates obtained using the maximum likelihood method. Another benefit is that also estimates of the single scattering density of unoccupied states are obtained which are useful for studying electronic structure effects and can be directly compared with life time broadened angular momen-
tum projected unoccupied density of states obtained from electronic-structure calculations. The obtained estimates of the unoccupied DOS are obtained without deconvolution and background removal, making them more reliable and intrinsically less noisy.

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