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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.

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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 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 ($\approx 100\,\mathrm{eV}$) 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]:

$$J(E_i) = \int_{E_i}^{E_{i+1}} M(E)N(E)\,\mathrm{d}E \tag{1}$$

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

$$M(E) = \int_{\Omega} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E}\,\mathrm{d}\Omega \propto \int_{\Omega} \frac{1}{q^2 E}\frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}\Omega \tag{2}$$

with

$$f(E,\mathbf{q}) = \sum_{|f\rangle} \frac{E}{q^2}\left|\langle i|\sum_{j}^{N} \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_j}|f\rangle\right|^2 \delta(E_i - E_f - E), \tag{3}$$

where $\mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}E$ is the double differential cross section and f is the generalised oscillator strength (GOS) for

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exciting an initial N-particle state $|i\rangle$ to all final states $|f\rangle$ with energy E_f, momentum transfer $\mathbf{q}$ and position coordinates of the atomic electrons r_j. For a single atom this becomes:

$$J_{\text{free}}(E_i) = \int_{E_i}^{E_{i+1}} M_{\text{free}}(E) N_{\text{free}}(E)\,\mathrm{d}E. \tag{4}$$

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

$$J_{\text{cryst}}(E) = \int_{E_i}^{E_{i+1}} M_{\text{cryst}}(E) N_{\text{cryst}}(E)\,\mathrm{d}E. \tag{5}$$

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 $\mathbf{q}$ [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:

$$J_{\text{cryst}}(E_i) = \int_{E_i}^{E_{i+1}} M_{\text{cryst}}(E) N_{\text{free}}(E) \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)}\,\mathrm{d}E, \tag{6}$$

$$J_{\text{cryst}}(E_i) \approx \int_{E_i}^{E_{i+1}} M_{\text{free}}(E) N_{\text{free}}(E) \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)}\,\mathrm{d}E, \tag{7}$$

$$J_{\text{cryst}}(E_i) \approx J_{\text{free}}(E_i) D(E_i) \tag{8}$$

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

$$D(E) = \frac{N_{\text{cryst}}(E)}{N_{\text{free}}(E)}. \tag{9}$$

$D(E)$ 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 Δl 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.

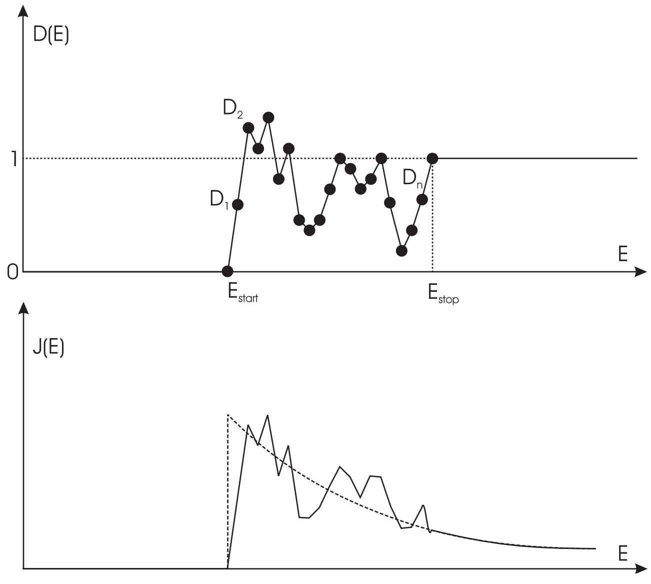

Fig. 1. Schematic drawing of the $D(E)$ function.

In practice E_{start} will be chosen just below the edge onset while E_{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_{start}, E_{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