Fitting the Momentum Dependent Loss Function in EELS

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ABSTRACT Momentum dependent inelastic plasmon scattering can be measured by electron energy loss in a transmission electron microscope. From energy filtered diffraction, the characteristic angle of scattering and the cutoff angle are measured, using a thin film of aluminum as a model test. Rather than deconvolving the data (as done in previous works), a fitting technique is used to extract the loss function from angular resolved spectra, starting from a simple model simulation. Microsc. Res. Tech. 74:212–218, 2011. © 2010 Wiley-Liss, Inc.

INTRODUCTION

The measuring and modeling of the loss function $\Im[-1/(\Delta q, E)]$ has constituted a field of research from past decades, also due to the improvement of theoretical frameworks for calculating the dielectric function (Batson and Silcox, 1983; Brosens et al., 1976, 1980; Devreese et al., 1980, 1983; Sturm and Oliveira, 1989). Their experimental results gave a good agreement if an exchange correction (Nozières and Pines, 1969) is taken into account in $x$, except at low $q$ values ($q < 0.75 \times 10^{10}$ m$^{-1}$). They attributed the discrepancy at low momentum transfer to the presence of interband transitions. Subsequent work was centered on measuring interband and intraband excitations and their mixing with the plasmon excitation, with the formation of the so called zone-boundary collective states (ZBCS) (Chen and Silcox, 1977; Sturm and Oliveira, 1989). Brosens et al. have performed an explicit calculation of the dynamical local field correction $G(q, E)$ in the so-called “Dynamical Exchange Decoupling” (hereafter denoted DED), using a variational approach to the time dependent Hartree-Fock equation (Brosens et al., 1976, 1980; Devreese et al., 1980, 1983). Their numerical results were compared with the experimental plasmon dispersion curve from a masterpiece work of Batson and Silcox (1983), taken at 75 keV incident energy. The main result was that dynamical exchange effects lower the slope of the plasmon dispersion, also in the case of aluminum, in agreement with the experiment. Schattschneider (1989) described in detail the dielectric picture of the loss function in the range of plasmons and interband excitations, together with the effects of a collection aperture and multiple scattering (Su and Schattschneider, 1992), and reported on the coherent double-plasmon excitation, using deconvolution techniques (Schattschneider et al., 1987), and recently measured also with inelastic X-ray scattering (Sternemann et al., 2005).

In this article, we show results on the angular dependence of inelastic scattering for plasmon excitations in the case of an interacting electron gas, which can serve as a model system for aluminum. First, we use energy filtered diffraction patterns to collect the signal as a function of momentum transfer $q$. The obtained characteristic angle $\theta_E$ and the cutoff angle $\theta_C$ are compared to predicted values. Then, we calculate the loss function in the $(q, E)$ plane according to the random phase approximation (RPA), or to the dynamical exchange decoupling (DED) as described by Devreese et al. (1983), and compare the results with the loss function determined by fitting the angular resolved spectra from the experiment, using the model simulation as a starting guess. The procedure represents a complementary way to the established deconvolution retrieval technique, similar to the method we used recently for extracting the single scattering distribution from core loss electron energy loss spectra (Verbeeck and Bertoni, 2009).

MATERIALS AND METHODS

Diffraction patterns and $(q, E)$ spectral maps from a polycrystalline Al film ($\approx 100$ nm thick) were obtained on a JEOL 3000F microscope at 300 kV, equipped with a FEG electron source and a Gatan GIF-2000 energy filter. Energy filtered diffraction images were taken with two different camera lengths, to explore very small angles (at 2.5 m nominal camera length, or a...
spectrometer collection half angle of 0.3 mrad), and large angles close to Bragg reflections (at 0.032 m nominal camera length or 25 mrad spectrometer collection angle). Two successive patterns taken at different exposures (one at 2 s and one at 200 s) were merged to permit the exploration of six orders of magnitude in the intensity of scattering. To obtain a diffraction pattern from the plasmon loss region, an energy shift of 18 eV was applied and a wide slit used (≥20 eV), to avoid artificial cut in the momentum distribution. A pattern from the elastic (and quasi-elastic) part was obtained with a filter width of 10 eV centered at 0 eV. For the (q, E) maps, multiple spectra were collected with the microscope in diffraction mode, allowing a careful measurement of the angle of acceptance of the spectrometer. A script obtainable from the authors permits the automatic acquisition of a series of spectra corresponding to different values of the projected momentum transfer (or Landau continuum), where particle-hole pairs can be excited (Egerton, 1996). Different values for the cut-off at around 5 mrad. This cutoff is related to the damping of a plasmon when it enters the continuum region (or Landau continuum), where particle-hole pairs can be excited (Egerton, 1996). Different values for the cut-

RESULTS

Angular Dependence of Scattering

In the first Born approximation (Egerton, 1996), the double differential cross section for an atom is given by

\[
\frac{d^2\sigma}{d\Omega dE} \propto \text{Im} \left[ \frac{1}{\delta(q, E)} \right],
\]

assuming

\[
E \ll E_0, \quad \theta \ll 1, \quad q \ll k_0.
\]

where E is the energy loss and \(E_0\) is the energy of the (fast) incoming electron. The expected angular distribution (neglecting the contribution from the loss function) is a Lorentzian function with half width at half maximum (HWHM) given by \(\theta_E\), the characteristic angle of scattering. This parameter can be measured taking a diffraction pattern filtered around the plasmon. We expect values below 0.05 mrad, so a big camera length is needed to avoid effects of the point spread function of the camera (or MTF). Also, the convergence angle must be reduced as much as possible (using close parallel beam illumination). In Figures 2a and 2b, the results of this measurement before and after deconvolution with the quasi-elastic diffraction pattern, are shown. The deconvolution undoes the effect of elastic and quasi-elastic (QE) scattering (i.e., thermal diffuse scattering or phonons). In this case, we need to do a 2D deconvolution in the q\(_\perp\) plane. We simply use a Fourier ratio (FR) method, described in Fourier space by

\[
I_{k}(q_{\perp}) = G(q_{\perp}) [I_M(q_{\perp})/I_M(q_{\perp})],
\]

where \(I_M(q_{\perp})\) is the plasmon filtered diffraction pattern, \(I_M(q_{\perp})\) is the quasi-elastic filtered pattern, and \(G(q_{\perp})\) is a gaussian function to reduce noise amplification when \(L_M\) becomes small (X denotes the Fourier transform of X). In this way, \(I_M(q_{\perp})\) should be dominated by plasmon inelastic scattering. As can be seen from Figures 2a and 2e, the deconvolution does not change considerably the pattern at low angles, indicating that at these angles the distribution was already dominated by inelastic scattering. The measured values for \(\theta_E\) are reported in Table 1, together with the expected values from the classical limit and a relativistic calculation. The effect of the quasi-elastic contribution is evident in Figures 2b and 2f, showing the angular distribution of scattering before and after deconvolution with the low-loss pattern \(L_M\). Figure 2b presents a diffuse background due to QE scattering. In Figure 2f, this background is reduced, revealing a smooth cutoff at around 5 mrad. This cutoff is related to the damping of a plasmon when it enters the continuum region (or Landau continuum), where particle-hole pairs can be excited (Egerton, 1996). Different values for the cut-

Fig. 1. The geometry of inelastic scattering in a transmission electron microscope. The angle θ is exaggerated for clarity.
off angle $\theta_C$ were proposed and discussed in the past, and their values are reported in Table 1, together with the experimental value determined in this work. A radial integration from Figure 2 is presented in Figure 3. The improvement after the deconvolution is evident. For the proposed values of $\theta_C$, the reader is referred to Egerton (1996), and references therein. Numerical values for $\theta_E$ and $\theta_C$ were estimated by fitting a rational function to the radially integrated profile. The measured value for $\theta_E$ is closer to the relativistic value, and the estimated value for $\theta_C$ is close to $0.74q_F/k_0$, the result obtained using Hartree-Fock wave functions by Ferrel (1957), predicting an abrupt cut off rather than the smooth one observed experimentally.

Fig. 2. Filtered diffraction patterns for the plasmon loss in aluminum, before (a and b), and after two dimensional Fourier-Ratio deconvolution (e and f) with a quasi-elastic pattern (c and d), measured at 2.5 m camera length (left), and at 0.032 m camera length (right). The right column shows the logarithm of the intensity to bring out more clearly the distribution of scattering in the low intensity region. The residual intensity on the left side in (f) is an artifact from a small misorientation induced by mechanical drift of the sample (due to the long time of acquisition for the pattern). It does not affect appreciably the distribution around the central spot.

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TABLE 1. Values for the characteristic angle of scattering $\theta_E$, and for the cut-off angle $\theta_C$, as proposed in literature (calc.), and measured (meas.) in this work

<table>
<thead>
<tr>
<th>Angle</th>
<th>Calc. (mrad)</th>
<th>Meas. (mrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_E = \frac{E_p}{2k_0}$</td>
<td>0.031</td>
<td>0.034 ± 0.002</td>
</tr>
<tr>
<td>$\theta_E = \frac{E_p}{2E_0}$</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>$q\nu/k_0$</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>$\nu = \frac{1}{(k_0q_0)}$</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>$\nu = \sqrt{2}/(E_0)$</td>
<td>7.83</td>
<td></td>
</tr>
<tr>
<td>$\nu = E_0/(h\nu k_0)$</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td>$\nu = 0.74q_0/k_0$</td>
<td>4.20</td>
<td>4.4 ± 0.2</td>
</tr>
</tbody>
</table>

Fig. 3. Radial intensity distribution for plasmon inelastic scattering in aluminum, as results from a radial integration of Figure 2: (raw data) from Figure 2a, (deconvolved) from Figure 2f. The result of the fit is also shown (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fitting the Loss Function

A specific momentum direction can be chosen looking in the back focal plane of the objective lens (see Fig. 1), where the diffraction pattern is formed. In Figure 4, we show the energy loss spectra for a scan with the scattering vector along the direction [33-1]. This direction was chosen so to have a Bragg reflection (corresponding to $\theta_B = 10.6$ mrad) far from the central spot. In this way, the elastic replica centered at the Bragg reflection does not influence the principal reflection considerably (see the discussion below). As it can be seen, the dominant features are the elastic and plasmon scattering processes, together with multiple scattering involving quasi-elastic processes (QE). The effect of these multiple processes on the measured spectra was first described in the work of Batson and Silcox (1983). They suggested a method to remove the effect of multiple scattering events by means of deconvolution. To perform the removal, they used a spectrum taken in image mode (i.e., integrated over a large range of $q$), to approximate the effect of quasi-elastic scattering and suitably normalized. The reader is referred to their work (Batson and Silcox, 1983) for the details [see Eq. (11) therein]. The image spectrum is subtracted from each spectrum of the scan (subtraction method). Furthermore, the deconvolution of the spectrum to obtain the single scattering term is made with a Misell-Jones method, reducing the spherically symmetric 3D problem ($q_x, q_y, E$) to a 2D problem ($q_y, E$), making use of Hankel transforms (or Fourier-Bessel transforms). The approach is correct (assuming circular symmetry for plasmon scattering in aluminum). To reduce possible errors in the integrations, they transformed an exponential approximating the Lorentzian function in Eq. (2). Modern algorithms improve convergence and precision for quasi-discrete Hankel transformation, using Bessel series. We use the symmetrization algorithm by Guizar-Sicarios and Gutierrez-Vega (2004) to transform Eq. (2), so to consider both the loss function and the Lorentzian term. Moreover, rather than deconvolving the data, we simulate the experimental spectra using fitting techniques, similar to the approach we successfully used in the case of core loss spectra (Verbeeck and Bertoni, 2006; Verbeeck and Van Aert, 2004). In the following procedure, an initial estimation of the loss function is obtained from a calculation. The loss function is considered as a matrix of parameters in the ($q, E$) plane. The matrix is passed to a fitting routine together with the function that calculates the model for the observed intensity $J_M(q, E)$ from the loss function. In this way, while reducing common noise amplification of deconvolution [i.e., better signal to noise ratio (SNR)], error estimates can be given. In our case, the fit iteratively optimizes the loss function using a nonlinear least squares minimization algorithm, finding the best estimate for the loss function. The principal steps for obtaining the measured intensity are the following:

- Calculate the loss function $\text{Im}[-1/\rho(q, E)]$, correctly weighted according to the second momentum sum rule, that can be written as (we are interested in relative intensities)
\[
\frac{\pi}{2\omega_p^2} = \int_0^\infty \text{Im} \left[ -\frac{1}{\varepsilon(q, E)} \right] E dE, \tag{5}
\]

where \(E_{\text{max}}\) is the numerical upper limit of integration (\(\sim 2.5\varepsilon_p\) in this case).

- Multiply it by the angular dependence of the inelastic process to obtain the single scattering inelastic term \(S(q, E)\),

\[
S(q, E) = \text{Im} \left[ -\frac{1}{\varepsilon(q, E)} \right] \ln \left( 1 + \frac{\Delta q^2}{q^2 + q^2_0} \right) / \ln \left( 1 + \frac{\Delta q^2}{q^2} \right), \tag{6}
\]

as results from Eq. (2), taking into account the effect of the finite entrance aperture of the spectrometer (\(\Delta q > k_0 q_p\) (Batson and Silcox, 1983).

- Calculate the multiple inelastic processes (Fig. 5c) as the exponential expansion

\[
\tilde{J}(\rho, \omega) = \exp(-t/\lambda) \exp \left[ \frac{t}{\lambda} \tilde{S}(\rho, \omega) \right], \tag{7}
\]

where \(\tilde{X}\) denotes the Fourier transform in energy \(E\) plus Hankel transform in momentum \(q\) of \(X\) (assuming circular symmetry in \(q\)), and \(t/\lambda\) is the thickness (as a fraction of the electron mean free path \(\lambda\)). \(\rho\) and \(\omega\) are the Fourier counterparts of \(q\) and \(E\). Note that Eq. (7) assumes the normalization of \(S(q, E)\) (i.e., \(\int S(q, E) dq dE = 1\)).

Fig. 5. Comparison between the calculated loss function \(\text{Im}(-1/\varepsilon(q, E))\) in the RPA, and in the DED, together with the retrieved loss function obtained by model-based fitting of measured spectra, using a convolution with a quasi-elastic profile (bottom left), and using the subtraction of an integrated spectrum (bottom right). The white lines define the continuum region.
• Calculate the quasi-elastic term $Q(q, E)$

$$Q(q, E) = \delta(E) d(q), \quad (8)$$

with $d(q)$ the angular profile of thermal diffuse scattering, that can be extracted from the experiment, so that $d(q) = J_M(q, E = 0)$. As can be seen from Figure 3, $d(q)$ is a wide angle scattering.

• Calculate the inelastic plus quasi-elastic scattering term $J_M(q, E)$ as

$$J_M(\rho, \omega) = J(\rho, \omega) J(\rho, \omega), \quad (9)$$

In all equations $q = |\mathbf{q}|$.

• The experimental resolution is added by convolution with a Gaussian function in $E$.

In this way, multiple processes involving inelastic events (plasmons and phonons) are taken into account. Note that we assume circular symmetry also for the quasi-elastic term $Q(q, E)$. This should be approximately true at small angle, so we extrapolate $d(q)$ to zero at high angles. A full 3D experimental map would be a better model, but would be extremely time consuming to record. We consider Eq. (9) a good approximation, especially if the Bragg spots are far away. The effect of a finite convergence angle $\alpha$ can also be taken into account in $\Delta q$ (considered as a total effective collection angle). A replica of the total scattering can also be produced at the Bragg angle ($2\theta_b$). The results of a fit on a $60 \times 24 (E, q)$ mesh for the loss function are shown in Figure 5. We report the 2D meshes as more representative for a whole comparison than separate plots of the loss function at different $q$. The plasmon dispersion is clearly visible, together with the damping of the plasmon at high values of the scattering vector. Clearly visible is also a double plasmon (P2) at around 30 eV, also dispersing. This is attributed to the double coherent plasmon (a simultaneous loss of 2$E_p$), instead of a double incoherent scattering of a plasmon [resulting from the convolution of the plasmon with itself, as described by Eq. (7)], confirming previous measurements using deconvolutions (Su et al., 1992). The intensity of the double plasmon P2 with respect to the single plasmon event as extracted from the obtained loss function is $\approx 6\%$. Another way to remove the quasi-elastic term is the one described by Batson and Silcox (1983) and also used by Su and Schattschneider (1992) in which an image spectrum (i.e., $q$ integrated) after normalization is subtracted from the experiment. A similar spectrum can be produced by the weighted sum of the spectra in $q$ (to consider for the circular integration in momentum of the detector when in image mode). The spectrum is subtracted from the experiment and $Q(q, E)$ is equal to 1 in Eq. (9). Note that in this case, a $-1$ is added to Eq. (7) so to exclude the unscattered beam. The loss functions obtained from a RPA calculation, and with dynamic exchange decoupling (DED), are also shown for comparison in Figure 5. The expression for RPA is obtained according to

$$e_{RPA}(q, E) = 1 + Q_0(q, E), \quad (10)$$

where $Q_0(q, E)$ is the Lindhard polarizability. In DED, the exchange and correlation term is calculated analytically (Devereese, 1983), and the dielectric function is expressed by

$$e_{DED}(q, E) = 1 + \frac{Q_0(q, E)}{1 - Q_0(q, E) G(q, E)}, \quad (11)$$

with $G(q, E)$ the exchange and correlation contribution (in the DED approximation). Several static local field corrections (Geldart et al., 1970; Hubbard, 1957; Singwi et al., 1968) are not explicitly discussed here, because their results do not appreciably differ from RPA in the high energy region. Apparently both RPA and DED approximations do not reproduce the observed loss function very well in the continuum region (defined by the white lines). They predict a (rather broad) maximum in the scattering amplitude in the continuum region. As a function of the wave vector $q$, this maximum in the DED approximation has a lower intensity as well as a lower energy position as compared to RPA, in better agreement with the experiment.

DISCUSSION

With energy filtered diffraction patterns we verified the parameters $\theta_b$ and $c$, and characterize the angular dependence of inelastic scattering, with a dynamic range of 6 decades, $\theta_b$ is in excellent agreement with the relativistic value corresponding to a Lorentzian angular distribution, and $c$ is very close to 0.74$q_E/k_0$, but smooth. These results can be used in the detailed characterization of partial coherence in inelastic scattering in holographic experiments, which is mainly determined by the angular dependence of scattering (Verbeeck et al., 2005; Verbeeck et al., 2008). Regarding the plasmon dispersion, the RPA model drastically overestimates the slope as a function of the wave vector. However, regardless the inclusion of dynamical exchange effects in the DED model substantially lowers this slope, it still does not give satisfactory quantitative prediction of the experimental scattering amplitude at large $q$. Both models predict a higher intensity for the onset of the continuum of particle-hole excitations with respect to the experiment, which can be related to the exclusion of lifetime effects. Figure 6 compares the width of the main feature in the loss function as measured from the result of the fit (experiment) and from the starting RPA and DED simulations. Of course the two models do not include the width of the collective mode (bulk plasmon), so a comparison is possible when its spectral intensity is transferred to the single particle region. The DED approximation gives quite good estimate of the width of the peak till $q \approx q_E$, despite the mixing of collective and single particle states of the excitation. This mixing behavior is evident at higher $q$, where both models diverge from the experiment. We have proposed a rigorous model based treatment to derive the bulk loss function from the experiment. We made use of 2D convolutions to include multiple scattering (incoherent) events in the model of the spectra, and reduce the noise amplification commonly linked to deconvolution. In our approach only the bulk losses are taken.
into account (as described by Eq. (7)). We do not consider surface losses that can interfere in multiple scattering events. The subtraction method has the advantage to approximately take into account a triple scattering event (bulk plasmon plus surface plasmon plus quasi-elastic), due to the fact that this is present in the image spectrum. The agreement between the two results has to be related to the low intensity of the surface plasmon in the experiment (about 0.03 with respect to the bulk plasmon), making the triple scattering event improbable. Both results present a non-negligible contribution to the loss function coming from double coherent plasmon excitation. The experimental results for the plasmon dispersion are similar to previous results in literature using deconvolution techniques (Batson and Silcox, 1983), with some differences. At large momentum transfer $q$ we found the maximum in the scattering amplitude at lower energy values, and at lower $q$ the onset in the continuum is more visible. The method can be applied to other materials where deviations between experiment and theory are most likely even bigger. A quantitative comparison is important to explore the deviations between theory and the loss function obtained from the experiment. A possible improvement to the presented theory would be including life-time broadening effects. On top of this, other effects can influence the loss function, as Cerenkov radiation, or interband transitions.

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