Scanning Microscopy

Volume 2 | Number 4 Article 13

10-18-1988

Coherence in Energy Loss Spectra of Plasmons

P. Schattschneider
Technische Universität Wien

P. Pongratz
Technische Universität Wien

Follow this and additional works at: https://digitalcommons.usu.edu/microscopy

 Part of the Life Sciences Commons

Recommended Citation

Schattschneider, P. and Pongratz, P. (1988) "Coherence in Energy Loss Spectra of Plasmons," *Scanning Microscopy*: Vol. 2 : No. 4 , Article 13.
Available at: https://digitalcommons.usu.edu/microscopy/vol2/iss4/13

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.

Scanning Microscopy, Vol. 2, No. 4, 1988 (Pages 1971-1978)
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

0891-7035/88$3.00+.00

COHERENCE IN ENERGY LOSS SPECTRA OF PLASMONS

P. Schattschneider* and P. Pongratz

Institut für Angewandte und Technische Physik, Techn. Univ. Wien

(Received for publication April 18, 1988, and in revised form October 18, 1988)

Abstract

Theoretical approaches to coherent excitation of two plasmons in a metal do not well agree with one another and with experimental results from electron energy loss spectrometry (EELS). We measured EELS spectra of polycrystalline aluminum films for various specimen thickness. By means of a new deconvolution method for multiple scattering, we obtained values between 0.6 % and 3.3 % for the probability F_2 of the coherent double plasmon event, relative to the single plamon event.

A review of earlier experimental as well as theoretical investigations is given. Our results together with a discussion of possible sources of error confirm our earlier findings that F_2 is much smaller than previously thought, and is thickness dependent. We found the available predictions of the effect unsatisfactory; a full theoretical treatment of the problem is still missing.

KEY WORDS: Electron energy loss spectroscopy (EELS), deconvolution, linear response, inelastic scattering, plasmons, plural scattering, coherence.

*Address for correspondence:
P.Schattschneider
Institut für Angewandte und Technische Physik
Techn. Univ. Wien
Wiedner Hauptstraße 8-10, A-1040 Wien, Austria
(0222) 58801 ext.5626

Introduction

Interpretation of electron energy loss spectra (EELS) is almost inevitably based on either of two linear relations:

- The proportionality of the scattering cross section $\partial^3 P_{\|}/\partial^2\Omega\partial E$ to the loss function $Im\left(\frac{1}{\varepsilon}\right)$ is the basic formula for interpretation of energy loss spectra in the low and medium energy loss range:

$$\partial^3 P/\partial^2\Omega\partial E = Im\left(\frac{1}{\varepsilon(\vec{q},\omega)}\right)/(e\pi a_0)^2 q^2. \qquad (1)$$

Here e is the elementary charge, a_0 is the Bohr radius and $q^2 = (\omega/v)^2 + k_\perp^2$. The incident electron has velocity v, the energy loss is $E = \hbar\omega$, and $k_\perp$ is related to the scattering angle ϑ as $k_\perp = k_0\vartheta$ where k_0 is the wavenumber of the incident electron. Once $Im(1/\varepsilon)$ is known, Kramers-Kronig-analysis (KKA) yields $Re(1/\varepsilon)$, and, eventually, $\varepsilon(\vec{q},\omega)$ can be derived.

- The second linear relation is the cross section's proportionality to the dynamical form factor $|S(\vec{q},E)|^2$

$$\frac{\partial^3\sigma}{\partial^2\Omega\partial E} = \left[\frac{2me^2}{(\hbar q)^2}\right]^2 \frac{k_b}{k_a}|S|^2 \qquad (2)$$

where m is the electron mass, and k_a, k_b are the wavenumbers of the fast probe electron before and after the interaction. Eq. (2) allows comparison with quantum mechanical predictions. Both these relations can be traced back to the assumption of strict linearity between the disturbance (the probing electron) and the response of the medium. In the classical approach which leads to Eq. (1) the electric field in the medium is assumed *linear* in the driving displacement field $\vec{D}$ of the electron. The linear response is described by a dielectric function $\epsilon(\vec{q},\omega)$

$$\vec{E}(\vec{q},\omega) = \epsilon(\vec{q},\omega)^{-1}\vec{D}(\vec{q},\omega). \qquad (3)$$

Eq. (2) is derived from the golden rule of perturbation theory which retains only the linear term in the Born series of the perturbed wave function $|\varphi>$.

$$|\varphi> = |\vec{k}_0> + G_0(\omega)W|\vec{k}_0> + (G_0(\omega)W)^2|\vec{k}_0> + \ldots = \sum_{n=0}^{\infty}(G_0(\omega)W)^n|\vec{k}_0> . \tag{4}$$

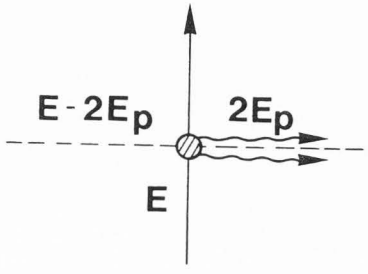
where $|\vec{k}_0>$ is the unperturbed free electron state. For sufficiently faint perturbation W, the series converges, since the higher the powers of G_0W, where G_0 is the Green operator, the smaller its contribution to the sum.

Linear response theories are good whenever the driving "force" is small. Strong electromagnetic fields, for instance, cause nonlinear effects—the theory of nonlinear optics celebrates the invalidation of linear response—and in quantum mechanics an interaction which is so faint as to justify a linear *ansatz* is the exception rather than the rule. As an aside, we mention that the dynamical theory of diffraction is also a nonlinear theory.

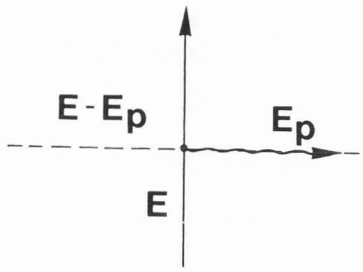
The reason for Eq. (1) being a good description for energy loss processes in the low energy range is that the Coulomb field of the electron is screened in the medium by polarization of the internal charges. On the other hand, the Born-Bethe formula (2) is successful when the velocity of the probe electron is much higher than the velocity of the target electrons, i. e. for fast probe electrons(Landau and Lifschitz 1979).

Why, then, is it important to look for nonlinear effects in EELS? The reason is primarily to find out how good an approximation is the linear response. Secondly, experiments which single out nonlinear effects can be compared with quantum mechanical higher order perturbation theory. Thirdly, such an investigation could ultimately answer the long-standing question whether and to what extent a combined dynamical-inelastic diffraction theory is useful.

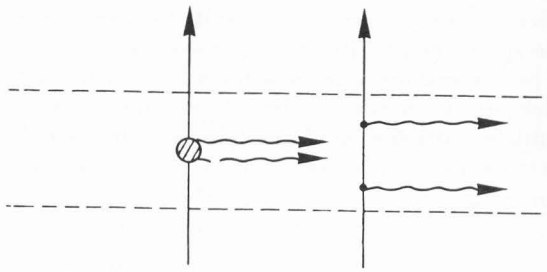
A good candidate for the search of nonlinear effects is the plasmon in metals since it has the highest excitation probability in the energy loss spectrum. Similar to nonlinear optics, we expect that effects quadratic in the driving field will cause some local maximum in EELS at twice the plasmon energy loss. The scattering process can be symbolized as



where the vertical arrow represents the trajectory of the probe electron, the dot is an effective interaction with the medium, which causes two quanta of plasma oscillation—the wiggly lines—to be emitted. The dashed line is the infinitely thin medium. The *linear* process looks like this:



A real specimen has always finite thickness, hence the following processes may occur:



Note that both processes cause the same energy loss of the fast probe, so they appear superimposed in EELS. Since process a) consists of two independent single plasmon excitations at different sites without phase relation, whereas b) comes about by correctly adding and multiplying quantum mechanical probability amplitudes, we shall refer to a) as *incoherent* and to b) as *coherent*.

As shown by Spence and Spargo (1971) the probability for the coherent process increases linearly with specimen thickness whereas that for the incoherent one increases with the thickness squared. Knowledge of the thickness dependence allows, in principle, to obtain the coherent contribution.

Experiments

In EELS-experiments, intensities of some ten to some hundred percent are found at the double plasmon energy loss, depending on the thickness of the specimen (Egerton 1986). This is because the fast electron traversing the specimen in an EELS-experiment interacts a number of times with the solid state plasma (an example for double scattering was given in the introduction); in each interaction along its trajectory it will loose the plasmon excitation energy E_p with a high probability, hence, the EEL-spectrum will exhibit a number of peaks at the multiples of the single plasmon excitation energy. The probability p_n for n-fold scattering obeys a Poisson distribution

for independent stochastic events (Raether 1980). Expressed as a function of energy loss E, the total scattering probability p is

$$p(E) = \sum_{n=0}^{\infty} p_n(E) = e^{-D} \sum_{n=0}^{\infty} \frac{D^n}{n!} g_n(E). \qquad (5a)$$

D is the thickness of the specimen in units of the mean free path λ of the fast electron in the medium,

$$\frac{1}{\lambda} = \sum_i \frac{1}{\lambda_i}, \qquad (5b)$$

where i denotes the different scattering mechanisms in the specimen (single plasmon, *coherent* double plasmon, phonon, core losses, etc.), and $g_n(E)$ are n-fold self-convolutions of the single scattering distribution $g_1(E)$ which results from all the possible mechanisms mentioned above. The distribution functions $g_n(E)$ are normalized to unity.

The problem is to single out the coherent contribution $g_1(2E_p)$ from the much larger $g_2(2E_p)D^2/2$. For convenience we abbreviate the probability for the coherent double plasmon loss *relative to the single plasmon loss* f_1 as F_2.

In the last two decades, there have been a few attempts to determine F_2 experimentally. This may be done either by evaluation of the thickness dependence of the measured intensity about the energy loss of $2E_p$ (Spence and Spargo 1971) or by removal of the incoherent events. A number of methods have been reported in the literature for retrieval of the single loss probability. Some of them are suited for EEL-spectra obtained in the electron microscope in *image mode*, i. e. when all electrons independent of their angle of scattering are collected (Johnson and Spence 1974, Misell and Jones 1969, Schattschneider 1983, Spence 1979).

More recently, methods have been used which work in *diffraction mode* (Misell 1970, Feldkamp et al. 1977). In the latter case, the scattering probability $p = p(E, \vartheta)$ is measured in the focal plane of the objective lens as a function of energy loss E and scattering angle ϑ.

By use of these methods for image mode spectra of aluminum F_2 was found to be less than 0.02 after correcting for incoherent double losses (Misell and Atkins 1971). Spence and Spargo (1974) reported a value below significance, which is less than 0.03 in their investigation. Batson and Silcox (1983) found $F_2 \sim 0.07$ after removal of plural incoherent losses in diffraction as well as image mode energy loss spectra of aluminum. The only other materials investigated in this respect are Mg and Sn (Blackstock et. al 1955, Spence and Spargo 1974). The latter authors report $F_2 = 0.07$ for Mg and $F_2 = 0.03$ for Sn, stating that the results are not conclusive for experimental reasons.

In an attempt to reconcile these contradictory results Schattschneider et al. (1987) investigated diffraction mode EEL-spectra of aluminum. For processing, they used a newly developed closed procedure capable of retrieving angle-resolved single inelastic scattering profiles from energy loss measurements (Schattschneider et al. 1985, Schattschneider 1986, Schattschneider et al. 1988).

The present results, including thicker specimens were obtained in image mode with a simplified processing routine (Schattschneider 1983).

From Figs. 1–4 it is evident that the coherent contribution F_2 increases with specimen thickness. Table 1 shows the various results obtained so far for aluminum.

authors	method	F_2	thickn.
	T/D/I	[%]	[MFP]
Blackstock et al. 1955	TD	≤ 4	~ 1
Misell & Atkins 1971	I	≤ 2	0.5–0.8
Spence & Spargo 1971	T	13	0.03–2.3
Spence & Spargo 1974	I	≤ 3	?
Batson & Silcox 1983	D/I	≤ 7	0.7–1.4
Schattschneider et al. 1987	D	0.5	0.5–1
Egerton (priv. comm.)	I	≤ 1	~ 1
present	I	0.6	0.5
present	I	0.9	1
present	I	1.3	2
present	I	3.3	4

Table 1: Excitation probability F_2 [%] of the coherent double–plasmon event in Al. Method applied is either investigation of the thickness dependence of the double plasmon maximum (T), diffraction mode (D) or image mode (I) electron microscopy. For error estimate of these values, see Tab. 2.

Discussion

Except for the results of Spence and Spargo, the F_2-values do not contradict one another, although the upper bounds given are quite different. The conspicuous high

value of $F_2 = 0.13$ has been obtained from EELS in a wedge-shaped single crystal, whereas all others used polycrystalline samples. It may well be that the diffraction conditions set up in a single crystal influence the Poisson statistics Eq. (5) by channeling or similar dynamical effects such that the analysis of the data based on independent events is not strictly valid. Moreover, the data of Spence and Spargo seem to indicate a thickness-*independent* intensity background at the double plasmon energy, contrary to the prediction.

Analysis of our new data shows that there are several possible sources of error:

- For thin specimens neglect of the surface plasmon contribution before processing may cause a small error in F_2, as shown in fig. 1.
- Neglect of zero loss deconvolution before processing causes an increase of 0.003 in F_2, see fig. 1. We estimate that this effect can, in extreme cases, be as large as some percent in F_2. The effect was discussed by Batson and Silcox (1983) who found the zero loss deconvolution necessary in order to remove quasielastic scattering from diffraction mode spectra. (This paper contains a wealth of information and practical hints on various corrections in EELS data processing).
- Detector saturation effects decrease the zero loss intensity. Consequently, the spectral intensity is overestimated which leads to oversubtraction at the double loss during plural scattering removal.
- Noise limits the accuracy of F_2 directly and by spectral processing.
- Variations of the thickness and/or small holes in the specimen cause deviations from the Poissonian distribution Eq. (5). A simulation of this effect shows that for reasonable assumption of thickness variations, F_2 is always overestimated. For the 100 nm-film a thickness variation of $\pm 20\%$ gives a spurious residual relative intensity $F_{spurious} = 0.007$.
- A number of experimental and processing errors the influence of which is difficult to estimate may also occur; such as current or voltage instabilities, spectrometer drift, growth of contamination layers *during* measurements, or numerical errors in processing the spectra. For our instrument and data processing, we estimate the combined effect of these influences to be on the order of ± 0.005.

As shown in Table 2, a direct comparison of the different results is not possible because unknown errors may be inherent in the previously reported data. Though, it is reasonable that exactly the influences mentioned above cause the large discrepancies in published data.

Theory

There are only two theoretical approaches to coherent double plasmon scattering. Ashley and Ritchie (1970) use second order perturbation theory in the interacting electron-gas. They give the expression

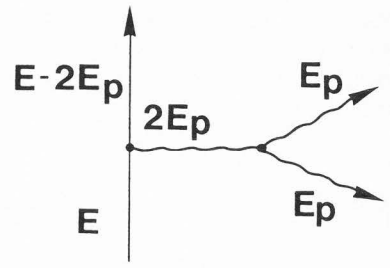
source	$D \leq 1$	$D = 2$	$D = 4$	max.
surf. pl.	0	0	0	~ 0.5
zero loss	0	0	0	~ 5
detector				
saturation	+0.3	+0.2	+0.2	~ 2
noise	± 0.1	± 0.1	± 0.4	± 1
thickn. var.	+0.5	+0.7	+0.4	~ 1
experiment	$+0.2/-0.4$	± 0.1	± 0.1	?
processing	± 0.3	± 0.2	± 0.2	?
sum total	$+1.4/-0.8$	$+1.3/-0.4$	$+1.3/-0.7$	≥ 9.5

Table 2: Sources and estimated magnitude of error in the coherent double–plasmon intensity F_2 [%], for aluminum films investigated by the authors (left three columns) and estimated maximum value for referenced data.

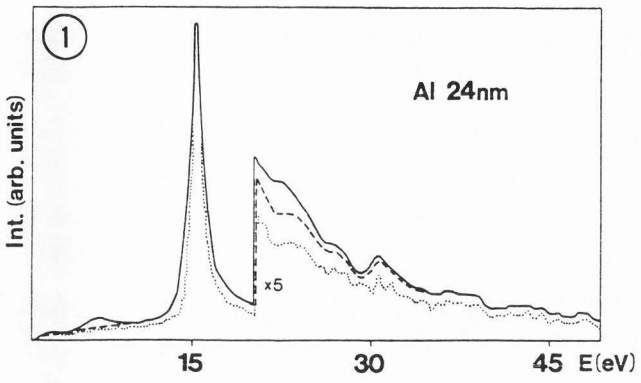
$$F_2 = \frac{9 k_c^5 \hbar^2}{2^7 \pi^2 n m_0 E_p}, \tag{6}$$

where k_c is the plasmon cutoff-wavenumber, n is the electron-density, m_0 the electron mass and E_p the plasmon energy. Expression (6) is very sensitive to the choice of k_c. For aluminum, one obtains $0.04 \leq F_2 \leq 0.17$ when $1.1\ \text{Å}^{-1} \leq k_c \leq 1.5\ \text{Å}^{-1}$.

Another, and maybe important question is which kind of scattering process enters this calculation. The relevant interaction can be symbolized as



This graph may be interpreted quite similar as the graphs given in the introduction, except that we are now



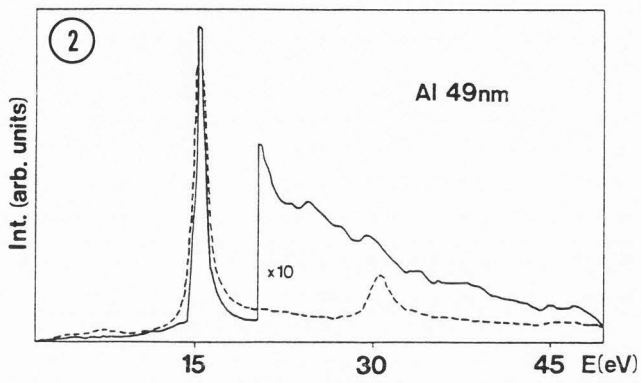
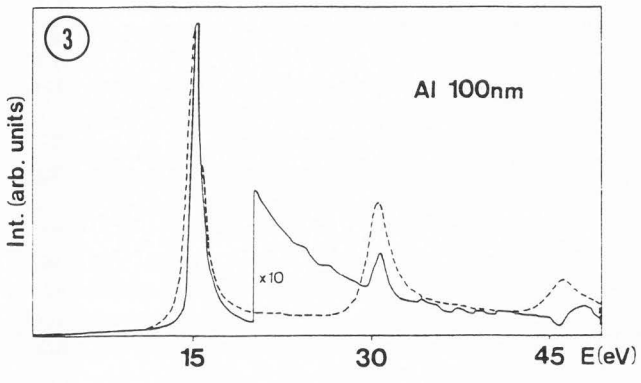


Fig. 1: Effects of neglect of surface terms and zero loss width in deconvoluted spectrum (Al, 24 nm). Full line: raw spectrum processed. $F_2 = 1.1\%$. Dashed line: surface loss removed before processing. $F_2 = 1.0\%$. Dotted line: Surface loss removed and corrected for zero loss width before processing. $F_2 = 0.7\%$.

Fig. 2: Measured spectrum (dashed) and deconvoluted spectrum for Al, 49 nm.



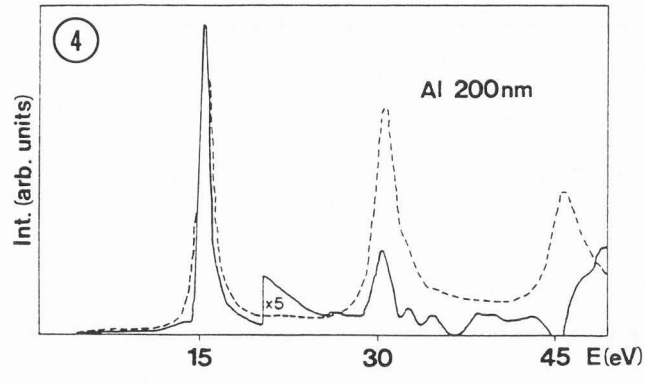
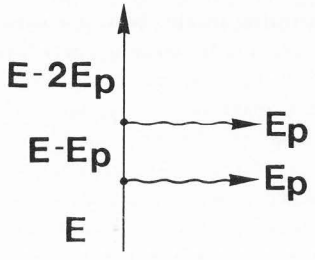


Fig. 3: Measured spectrum (dashed) and deconvoluted spectrum for Al, 100 nm.

Fig. 4: Measured spectrum (dashed) and deconvoluted spectrum for Al, 200 nm.

dealing with quantum mechanical *probability amplitudes*. The fast electron of energy E creates one (virtual) plasmon of energy $2E_p$ which decays into two real quanta subsequently.

The second theory is a semiclassical one. Lucas and Sunjič (1972) calculate quantum mechanically the n-fold excitation probability of a harmonic oscillator which is passed by a fast electron. They derive the probability of coherent multiple excitations of the oscillator, which should cause a Poissonian distribution of equidistant δ-like maxima in EELS. To establish a connection to the previous approach, the process considered here is



which is different from the calculation of Ashley and Ritchie (1970). So it is perhaps no surprise that the two theories predict different values for F_2.

Furthermore, it is questionable whether a plasmon resembles the excited state of a harmonic oscillator, and the extension of this theory to wavenumber-dependent excitations is not straightforward. Following Lucas and Sunjič (1972), the expression

$$F_2 = d \cdot \frac{\alpha n e^4 \pi}{2 E_p E_0} ln(1 + (\frac{v k_c}{\omega})^2) \qquad (7)$$

for F_2 can be derived. Here, α is the dispersion coefficient of the plasmon. E_p, E_0 are the plasmon energy and the kinetic energy of the probe electron, n is the electron density in the target, and d is the length scale over which the target electrons oscillate coherently. Taking published values for aluminum (Raether 1980) and our recent experimental findings, we obtain from Eq. (7) a thickness dependent coherence length for the four specimens. For increasing film thickness $d = 15\,nm, 22\,nm, 32\,nm, 82\,nm$.

In the $200\,nm$–Al–film, this would mean that a sphere of $\sim 80\,nm$ diameter participates in the plasma oscillation. For specimens of lesser thickness the coherent volume would be reduced, resulting in a decrease of F_2. This is a possible, but not conclusive explanation of the thickness-dependence in our values for F_2 since in the derivation of Eq. (7) the momentum-dependence of the loss process was neglected; an assumption which is certainly a very rough approximation but should at least give the correct order of magnitude of the effect.

Conclusions

After having given a rationale for the search of non-linear effects in EELS, we reviewed the experimental and theoretical findings on coherent double-plasmon excitation. New results for aluminum, together with a discussion of possible sources of error confirm our earlier findings that F_2 is much smaller than previously thought. We found the available predictions of the effect unsatisfactory; a full theoretical treatment of the problem is still missing. Apart from the theoretical viewpoint, the problem of coherence in plasma oscillations may also be of practical importance since the plasmon-electron coupling (and this is what F_2 essentially measures) is one of the candidates for explanation of high T_c-superconductivity.

Acknowledgements

This work was sponsored by the Jubiläumsfond der Stadt Wien. We are indebted to F. Födermayr and to D. – S. Su for assistance in measurements and processing of spectra.

References

Ashley JC, Ritchie RH. (1970). Double-Plasmon Excitation in a Free-Electron Gas. Phys.Stat.Sol.38, 425-434.

Batson PE, Silcox J. (1983). Experimental energy-loss function, Im[-1/$\varepsilon(q,\omega)$], for aluminum. Phys. Rev. B27, 5224-5239.

Blackstock AW, Ritchie RH, Birkhoff RD. (1955). Mean Free Path for Discrete Electron Energy Losses in Metallic Foils. Phys. Rev. 100, 1078-1083.

Egerton RF. (1986). Electron Energy–Loss Spectroscopy in the Electron Microscope, Plenum Press, New York, chapter 4.

Feldkamp LA, Davis LC, Stearns MB. (1977). Analysis of electron inelastic-scattering data with application to Cu. Phys.Rev.B15(12), 5535-5544.

Johnson DW, Spence JC. (1974). Determination of the single-scattering probability distribution from plural-scattering data. J.Phys.D 7, 771-780.

Landau LD, Lifschitz EM. (1979). Lehrbuch der theoretischen Physik III. (Theoretical PhysicsIII). Akademie-Verlag Berlin. 599ff.

Lucas AA., Sunjič M. (1972). Fast–electron spectroscopy of collective excitations in solids. Pergamon press, Oxford. 83ff.

Misell DL, Atkins AJ. (1971). An attempt to observe the double plasmon loss by electron spectroscopy. J. Phys. C4, L81-L84.

Misell DL, Jones AF. (1969). The determination of the single-scattering line profile from the observed spectrum. J.Phys.A Ser.2, Vol.2, 540-546.

Misell DL. (1970). The Calculation of Optical Data from Electron energy Loss Measurements. Z.Physik 235, 353-359.

Raether H. (1980). Excitation of Plasmons and Interband Transitions by Electrons. Springer–Verlag Berlin. 40 ff.

Schattschneider P. (1983). Retrieval of single loss profiles from energy loss spectra. A new approach. Phil.Mag. B47, 555-560.

Schattschneider P, Zapfl M, Skalicky P. (1985). Hybrid deconvolution for small-angle inelastic multiple scattering. Inverse Problems 1, 381-391.

Schattschneider P. (1986). Fundamentals of inelastic electron scattering. Springer Verlag Wien, N.Y. chapt.8, .

Schattschneider P, Födermayr F, Su DS. (1987). Coherent Double-Plasmon Excitation in Aluminum. Phys. Rev. Lett. 59, 724-727.

Schattschneider P., Födermayr F., Su DS. (1988). Deconvolution of plasmon spectra. Scanning Microscopy Suppl. 2, 1988, 255-259.

Spence JC, Spargo AE. (1971). Observation of double-plasmon exctitation in aluminium. Phys. Rev. Lett. Vol.26 No.15, 895-897.

Spence JC, Spargo AE. (1974). Measurement of the double plasmon probability. Proc. 8. Int. Conf. Electron Microscopy, Canberra, 390-391.

Spence JC. (1979). Uniqueness and the inversion problem of incoherent multiple scattering. Ultramicroscopy 4, 9-12.

Discussion with reviewers

R. F. Egerton: What approximations are made in the deconvolution procedure? How was the instrumental energy-resolution function obtained: from the zero loss peak, or by recording the response with no specimen? Is it possible that the residual peak at $E = 2E_p$ (which increases with specimen thickness) could be due to small errors in the knowledge of the response function?

P. Batson: How might one go about including the surface scattering in the basic formalism to remove the need for approximate removal procedures?

Authors: There is only one approximation *in* the deconvolution procedure: Replacement of an integral equation by an algebraic (matrix) equation, which has an experimental counterpart in replacing a continuous spectrum by a discrete one. In order to deliver sensible results, the procedure expects a spectrum from a specimen of uniform thickness (not necessarily homogeneous), no surface

contributions and an ideal δ-like response. For the influence of thickness variations see Table 2. The surface plasmon was deconvolved approximately for the $24\,nm$ and the $49\,nm$ thick specimens, and neglected for the thicker ones. We do not believe that it is possible to include the surface term in some basic formalism—in the sense that the single loss function or the dielectric function can be obtained by a noniterative solution of some formula.

The instrumental function was obtained by recording with no specimen. Deconvolution with a response function redistributes intensity in the spectrum, without changing the ratio of areas under well-defined excitations, as long as the resonant energies are sufficiently apart. It follows that small errors in the response function will cause errors in the shape of the processed spectra, but not so in the ratios of the integrated intensity of the double (triple, multiple) to the single plasmon loss.

P. Batson: The figures show that the statistical quality and reproducibility of the single scattering results are not very good. Also, non-physical effects are present. For instance, your results show anomalous peaks at the third plasmon energy near $45\,eV$. What causes the non-physical result? How can we trust the intensity at $30\,eV$ in the face of the gross variation at $45\,eV$?

R. F. Egerton: What is the cause of the "fine structure" which is visible (after deconvolution) between the plasmon peaks in Figs. 1-4?

C. Colliex: About the results and figures, it is not clear how you measure your "relative probabilities" as a function of thickness: could you introduce some more quantitative values on the vertical scale? Is there a possibility for estimating the signal-to-noise? For instance about triple loss there seems to be a strange behaviour after deconvolution: no contribution for $24\,nm$, a slight positive one for $49\,nm$ and an increasing negative one for $100\,nm$ and $200\,nm$. In this latter case, the noise seems as important as the F_2 signal.

Authors: It is an inherent feature of our deconvolution procedure that the measured spectrum is internally normalized (to $e^D - 1$), so the vertical scale is neither counts nor probabilities. We decided to use the notation "arbitrary". The relative probabilities as given in Table 1 were measured by integrating the spectra from $E_{min} = n\,E_p - 2\,eV$ to $E_{max} = n\,E_p + 3\,eV$, and $n = 1$ or $n = 2$.

The signal-to-noise ratio was estimated from the counting statistics (the number of counts at the plasmon maximum was between 3700 and 51000 for the four specimens) and its effect on F_2 is given in Table 2.

The behaviour of the triple loss can be understood as follows: Owing to truncation effects in the multiplication of matrices the channels with highest energy loss ($\sim 47\,eV$) are not reliable. Moreover, discretization causes small errors (less than $0.2\,eV$) in the position of any plasmon maximum. The deconvolution is, in its essential part, a subtraction of the weighted, self-convoluted maximum at $15\,eV$ from the spectrum. In the process of self-convolution a small error in the peak position increases by a factor of three for the triple loss. The subtraction of maxima which can be misaligned by as much as $0.8\,eV$ results in the oscillatory behaviour ("fine structure") visible in Figs. 3, 4. Though, the *area* under any peak is not much influenced by misalignment, so we can trust the results within the limits given in Table 2.

For the thickest film, the noise at the triple plasmon loss can be estimated from counting statistics as $\sim 1.5\%$ of the overall maximum. This is of the same order of magnitude as the oscillations between the maxima, but undoubtedly smaller than F_2.

C. Colliex: What is the difference between the first graph in the Theory section and the first graph in the Introduction?

Authors: The process symbolized by the former is one of the many processes contained in the latter.

C. Colliex: You introduce an important parameter d which is the length scale over which the target electrons oscillate coherently. Could you explain it more clearly? I do not understand why it is thickness dependent.

Authors: Following the theory of Lucas and Sunjič (1972) the number of coherently oscillating electrons determines F_2. Given the electron density, a coherence length can be calculated which should—naïvely thinking— either equal the film thickness or be constant. A tentative explanation is that scattering at the grain boundaries in the specimen sets up a state of partial coherence. To our knowledge, there is no theory elaborate enough to really explain nonlinear effects in collective excitations, not to speak of a coherence length.

C. Colliex: On the figures in the Introduction, can you comment about the fact that you use a dot for single plasmon scattering and a dashed circle of given extent for double plasmon excitation. Any idea of a correlation length?

Authors: Those graphs are meant symbolically. The shaded circle denotes that a number of interrelated and entangled processes take place in this interaction. If you like it, you can think of the diameter of the circle as a measure of complexity! The correlation length—if this is meant to be the length scale over which the moving electrons are correlated—equals the coherence length defined in the Theory section.

C. Colliex: What is the expected lifetime of the double plasmon and what are the consequences on the energy width of this feature in the spectrum: will there be a peak at $2E_p$ or a rather broad, flat (and thus invisible) band?

Authors: In the theory of Lucas and Sunjič (1972) plasmons have infinite lifetimes. In the quantum mechanical approach of Ashley and Ritchie (1970) a lifetime could in principle be calculated from the imaginary parts of the poles of the Green function, however, no one has ever set out for such a calculation. In case of a long-lived state of two simultaneously excited plasmons, there should be

a binding energy, shifting the two-plasmon maximum to lower energies. We could not observe anything of this kind, in agreement with earlier work—e. g. Batson and Silcox (1983).