Quantitative analysis of reflection electron energy-loss spectra

ARTICLE *in* SURFACE AND INTERFACE ANALYSIS · JANUARY 1986

Impact Factor: 1.25 · DOI: 10.1002/sia.740190152

2 AUTHORS:

Francisco Yubero
Spanish National Research Council
184 PUBLICATIONS **2,550** CITATIONS
SEE PROFILE

Sven Tougaard
University of Southern Denmark
216 PUBLICATIONS **5,416** CITATIONS
SEE PROFILE

SURFACE AND INTERFACE ANALYSIS, VOL. 19, 269–273 (1992)

Quantitative Analysis of Reflection Electron Energy-loss Spectra

F. Yubero* and S. Tougaard
Fysisk Institut, Odense Universitet, DK-5230 Odense M, Denmark

It is shown that a quantitative description of the energy-loss processes in a reflection electron energy-loss spectroscopy (REELS) experiment cannot be obtained from a simple linear combination of pure bulk and pure surface components. A quantitative description can, however, be obtained within the dielectric response formalism for a more realistic model which takes into account the physical conditions in a REELS experiment.

INTRODUCTION

Reflection electron energy-loss spectroscopy (REELS) spectra carry information on the inelastic scattering cross-sections for electrons in solids, they are easily measured and the experimental facility is available on most surface science equipment.[1–5] However, realistic models are required to extract quantitative information, such as inelastic scattering cross-sections, and they are also important for quantitative analysis or XPS and AES.[6]

For an infinite medium the cross-section $K(E_0, \hbar\omega)$ may be evaluated directly from the complex dielectric function ε.[7,8] However, in XPS, AES and REELS the effect of the surface causes the effective cross-section to deviate from that of an infinite medium. It has been suggested[1–4] that the combined effect of the surface and the bulk excitations be modelled by making a linear combination of the surface electron loss function $\mathrm{Im}\{-1/(\varepsilon+1)\}$ and the bulk electron loss function $\mathrm{Im}\{-1/\varepsilon\}$.

The purpose of this paper is to study the validity of this assumption. It is found that a reasonable fit of the cross-sections at different energies can be obtained in this way, but it is also found that the fitting parameters carry little quantitative information. The application of improved quantitative models is discussed and it is shown that the cross-section cannot be separated into pure surface and bulk contributions. This is due to the importance of electron momentum transfer and to the interference between the field created by the incoming electron and the outgoing electron. A model which takes these effects into account provides a *quantitative* description of REELS with reasonable accuracy.

METHOD OF ANALYSIS

From experimental REELS spectra we can remove multiple scattering effects and determine the product $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ of the inelastic electron mean free path $\lambda(E_0)$ and the inelastic scattering cross-section $K(E_0, \hbar\omega)$.[5,9] We want to investigate the validity of a model in which $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ is expressed as a linear combination of the bulk electron loss function $\mathrm{Im}\{-1/\varepsilon(\omega)\}$ and the surface electron loss function $\mathrm{Im}\{-1/(\varepsilon(\omega)+1)\}$, where $\varepsilon(\omega)$ is the dielectric function of the medium.

First we have to find $\mathrm{Im}\{-1/\varepsilon\}$. To this end, we assume that $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ at high primary energy E_0 is proportional to $\mathrm{Im}\{-1/\varepsilon\}$ (i.e. we neglect the surface contribution)

$$\lambda(E_0) \cdot K(E_0, \hbar\omega) = C \cdot \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} \tag{1}$$

To find the proportionality constant C we use the sum rule[10]

$$P \int_0^\infty \frac{\mathrm{d}\hbar\omega}{\hbar\omega} \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} = \frac{\pi}{2} \tag{2}$$

where P indicates the Cauchy principal part of the integral. Then, from Eqns (1) and (2) we get

$$C = \frac{2}{\pi} P \int_0^\infty \frac{\mathrm{d}\hbar\omega}{\hbar\omega} \lambda(E_0) \cdot K(E_0, \hbar\omega) \tag{3}$$

The next step is to use the Kramer–Krönig relations to find $\mathrm{Re}\{1/\varepsilon(\hbar\omega)\}$[10]

$$\mathrm{Re}\left\{\frac{1}{\varepsilon(\omega)}\right\} = 1 - \frac{2}{\pi} P \int_0^\infty \frac{\hbar\omega' \, \mathrm{d}\hbar\omega'}{(\hbar\omega')^2 - (\hbar\omega)^2} \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega')}\right\} \tag{4}$$

Then, the dielectric function is given by

$$\varepsilon(\omega) = \frac{\mathrm{Re}\{1/\varepsilon(\omega)\} + i\mathrm{Im}\{-1/\varepsilon(\omega)\}}{[\mathrm{Re}\{1/\varepsilon(\omega)\}]^2 + [\mathrm{Im}\{-1/\varepsilon(\omega)\}]^2} \tag{5}$$

At lower primary energies E_0 we assume that within this simple model

$$\lambda(E_0) \cdot K(E_0, \hbar\omega) = C_B \cdot \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} + C_S \cdot \mathrm{Im}\left\{\frac{-1}{(\varepsilon(\omega)+1)}\right\} \tag{6}$$

* Permanent address: Departamento Física Aplicada C-XII, Universidad Autónoma de Madrid, E-28049 Madrid, Spain.

0142-2421/92/240269-05 $07.50

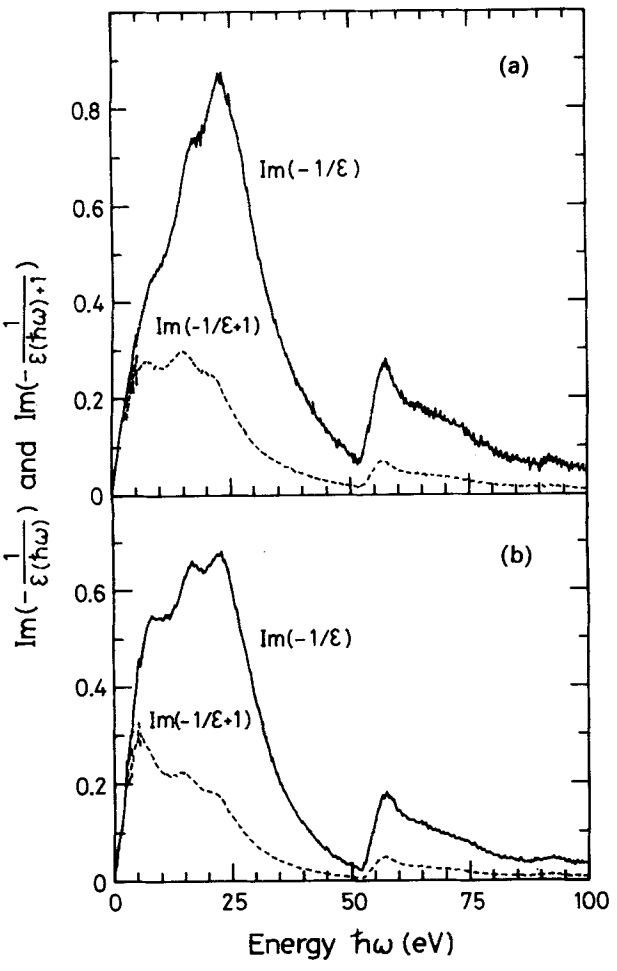

Figure 1. Bulk electron loss function $\mathrm{Im}\{-1/\varepsilon\}$ for Fe determined from Eqns (1)–(3) (full line) and the corresponding surface electron loss function $\mathrm{Im}\{-1/(\varepsilon+1)\}$ (dotted line). $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ in eqn (1) was taken from experimental REELS[5] at $E_0 = 10\,000$ eV in (a) and at $E_0 = 2000$ eV in (b).

Finally, a least-squares fit to the experimental $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ determines the values of C_B and C_S.

RESULTS

The REELS spectra have been measured with several primary electron energies ($E_0 = 10\,000$, 2000, 1000 and 300 eV).[5] The REELS spectrum contains contributions from multiple inelastic electron scattering. To correct for these effects and thereby to determine $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ we have used the algorithm developed by Tougaard *et al.*[9]

$$\lambda(E_0) \cdot K(E_0, E_0 - E) = \frac{1}{c}\left[j_1(E) - \int_E^{E_0} \lambda(E_0) K(E_0, E' - E) j_1(E')\, \mathrm{d}E'\right] \quad (7)$$

where $j_1(E)$ is the experimental spectrum, $\lambda(E_0)$ the inelastic electron mean free path, $c = \int_{E_0^-}^{E_0^+} j_1(E)\, \mathrm{d}E$ is the area of the elastic peak and $E_0 - E = \hbar\omega$.

Inelastic electron scattering cross-sections for Fe were determined in this way for the above-mentioned primary electron energies (see Ref. 5). We then performed the following two sets of fits.

For the spectrum taken at 10 000 eV we expect the contribution from surface excitations to be small. Therefore, it is a reasonable approximation to neglect surface excitations and apply Eqns (1)–(3) to determine the bulk electron loss function $\mathrm{Im}\{-1/\varepsilon(\omega)\}$. Finally, the surface loss function $\mathrm{Im}\{-1/(\varepsilon(\omega)+1)\}$ is determined by the procedure outlined in the previous section. The result is shown in Fig. 1(a).

These functions were used to make the best least-squares fit by eqn (6) to the experimental cross-sections, and the constants C_B and C_S were determined for the various primary energies as shown in Table 1. The fitted curves as well as the experimentally determined cross-sections are shown in Fig. 2(a).

We would expect the quality of the fit to be worse if $\mathrm{Im}\{-1/\varepsilon(\omega)\}$ is determined by Eqn (1) from an experimental cross-section taken at a lower primary energy because of the expected increase in the importance of surface excitations. To study whether this behaviour is reflected by the model, we have made a similar analysis using the cross-section determined at 2000 eV on the left-hand side of Eqn (1). The results are shown in Figs 1(b) and 2(b) and Table 1. The energy of 2000 eV was chosen because most electron spectrometers in surface analysis equipment only operate up to ~2000 eV.

Table 1. Values of C_B and C_S in Eqn (6) used for the fitted curves in Fig. 2(a) and 2(b)

	(a)			(b)		
E_0(eV)	C_B(eV^{-1})	C_S(eV^{-1})	r_s[a]	C_B(eV^{-1})	C_S(eV^{-1})	r_s[a]
10 000	0.0327	0	0	—	—	—
2000	0.0153	0.0437	0.49	0.0359	0	0
1000	0.0023	0.0886	0.93	0.0212	0.0550	0.50
300	−0.0141	0.1184	1.55	−0.0042	0.1106	1.13

[a] r_s is the fraction of surface contribution.

DISCUSSION

The quality of the fit based on $\mathrm{Im}\{-1/\varepsilon\}$ determined from $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ at 10 000 eV (Fig. 2(a)) is clearly worse than the fit (Fig. 2(b)) based on $\mathrm{Im}\{-1/\varepsilon\}$ from $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ at 2000 eV. This result indicates that the formalism described here is not valid, since surface excitations must be larger at lower primary energy and Eqn (1) must be most accurate when $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ at 10 000 eV is used.

To estimate the relative surface to bulk contribution to the $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ functions we have to take into account that the area of $\mathrm{Im}\{-1/\varepsilon\}$ is different from the area of $\mathrm{Im}\{-1/(\varepsilon+1)\}$ by a factor $f = 2.97$ in Fig. 1(a) and $f = 3.05$ in Fig. 1(b). From the data in Table 1 we then find the fraction of surface contribution $r_s = C_s/(C_s + f \cdot C_b)$, which is also shown in Table 1.

We can compare this to results for Al where the surface and bulk excitations are clearly separated. From previous results (see fig. 2 in Ref. 9) we can then estimate that at 1000 eV and 300 eV primary electron energy the fraction of surface contribution to $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ for Al is ~0.3 and ~0.6, respectively. This is quite different from the results obtained for Fe in Table

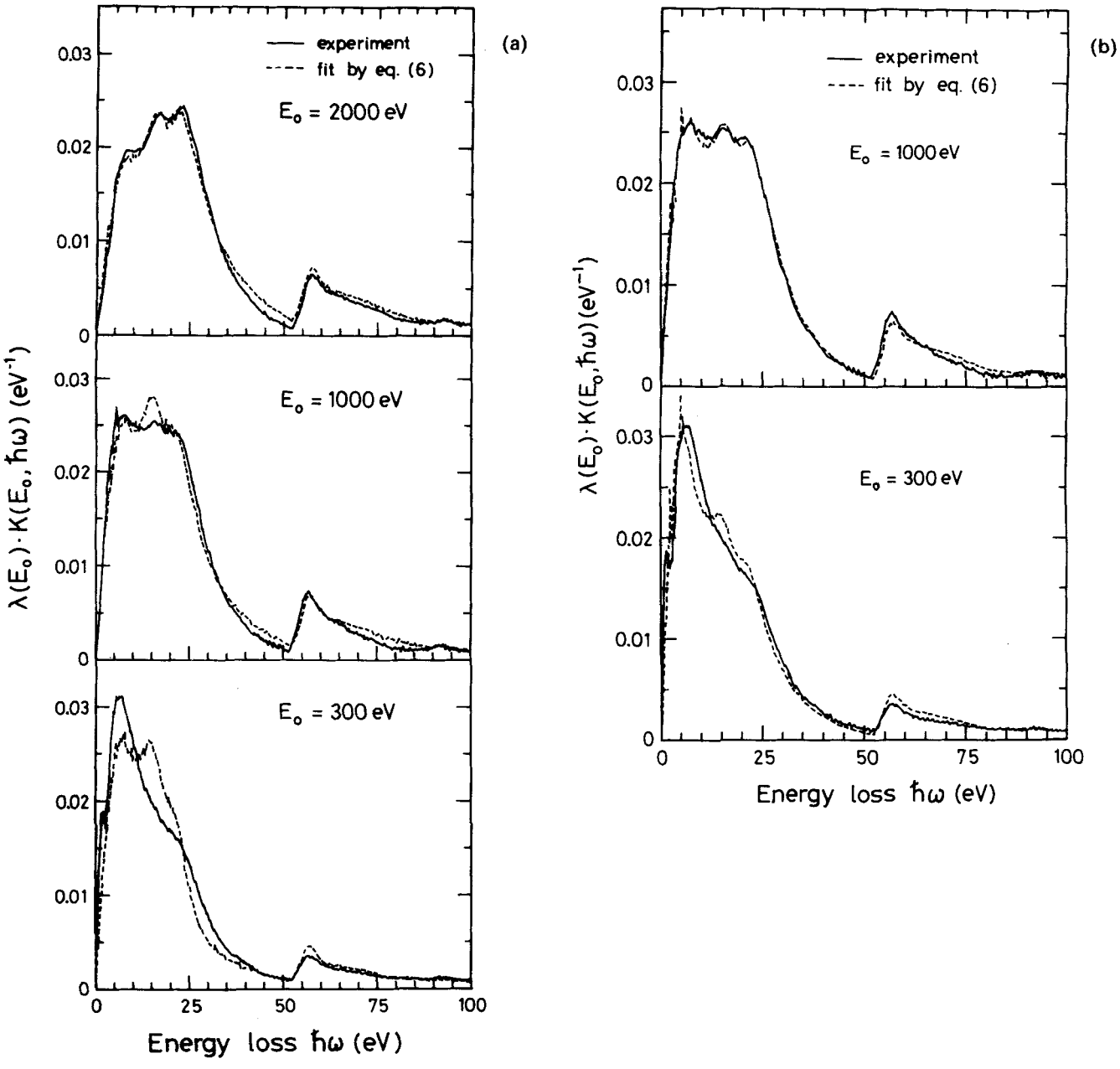

Figure 2. $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ in Fe at various primary electron energies E_0 determined from experimental REELS spectra by eqn (7) (full lines) and the least-squares fits obtained by eqn (6) with the parameters C_B and C_S in Table 1. In Fig. 2(a) the functions $\mathrm{Im}\{-1/\varepsilon\}$ and $\mathrm{Im}\{-1/(\varepsilon+1)\}$ were determined from REELS cross-sections[5] at 10000 eV (Fig. 1(a)), and in Fig. 2(b) they were determined at 2000 eV (Fig. 1(b).

1, where the fraction of surface contributions are much larger. Furthermore, to reproduce the cross-sections for Fe at 300 eV non-physical fitting parameters with negative bulk contribution are needed.

These results show that the simple model described here cannot be applied for a quantitative description of electron energy-loss processes in the surface region of solids.

We believe that the reasons for these deficiencies of the simple model outlined here are partly that the effect of momentum transfers have not been included and partly that it is necessary to consider more detailed models which describe the interaction between the fast electron and the surface of the solid.

The electron energy-loss processes experienced by the electron depends on the depth below the surface reached by the electron before it is back-reflected. Therefore, we have to consider the effective inelastic scattering cross-section $K_{\mathrm{eff}}(E_0, \hbar\omega, x)$, defined as the average energy loss over the travelled pathlength inside the solid per unit pathlength and per unit energy loss.

To calculate $K_{\mathrm{eff}}(E_0, \hbar\omega, x)$ we have developed a model within the dielectric response formalism which takes into account the effect of electron momentum transfer and the interference between the field created by the incoming electron and the outgoing electron.[11] Within this model Fig. 3 shows $K_{\mathrm{eff}}(E_0, \hbar\omega, x)$ for electrons of 2000 eV and 300 eV in Fe for different pathlengths x. It is clear that $K_{\mathrm{eff}}(E_0, \hbar\omega, x)$ does not consist of just a surface and a bulk component but of several peaks. The energy position and the width of the

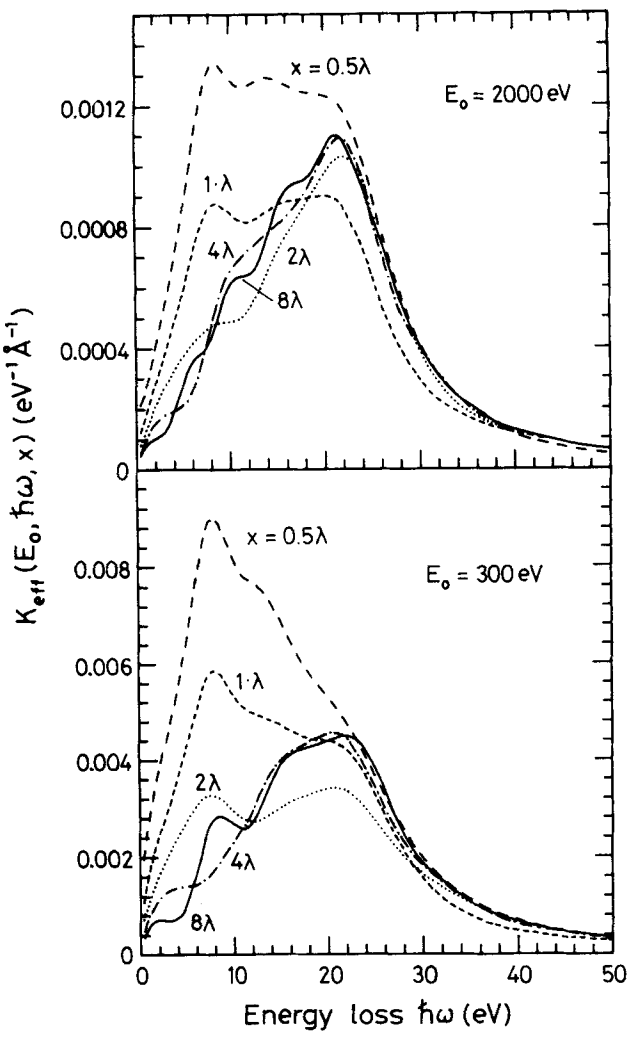

Figure 3. The effective inelastic electron scattering cross-section $K_{eff}(E_0, \hbar\omega, x)$ calculated by the model in Ref. 11 at $E_0 = 300$ eV and $E_0 = 2000$ eV for different pathlengths travelled by the electron in Fe. The pathlengths are given in units of $\lambda = 7.2$ Å at 300 eV and $\lambda = 27.7$ Å at 2000 eV.[13]

peaks vary considerably with primary energy and pathlength.

The cross-section determined from a REELS experiment (by Eqns (7)) is a weighted average over $K_{eff}(E_0, \hbar\omega, x)$ for all pathlengths x. A quantitative description can thus not be expected with the simple model here and the assumption in Eqn (6) of only a pure surface and a pure bulk component.

On the basis of the model in Ref. 11, we have also evaluated theoretical cross-sections for comparison with the experimental cross-sections (for details see Ref. 11). The results for Fe are shown in Fig. 4 at 10 000 eV, 2000 eV and 300 eV primary electron energy. The only input in these calculations is the dielectric function (taken from Ref. 12) and the inelastic mean free path (taken from Ref. 13). Thus, no adjustable parameters have been applied. In spite of this, the *quantitative* agreement between theory and experiment is reasonable.

The dielectric function for Fe in these calculations was taken as a fit to optical data[12] that unfortunately only are available in the energy range 0–30 eV. Improved agreement between theory and experiment in Fig. 4 might be expected with a more complete dielectric function for Fe.

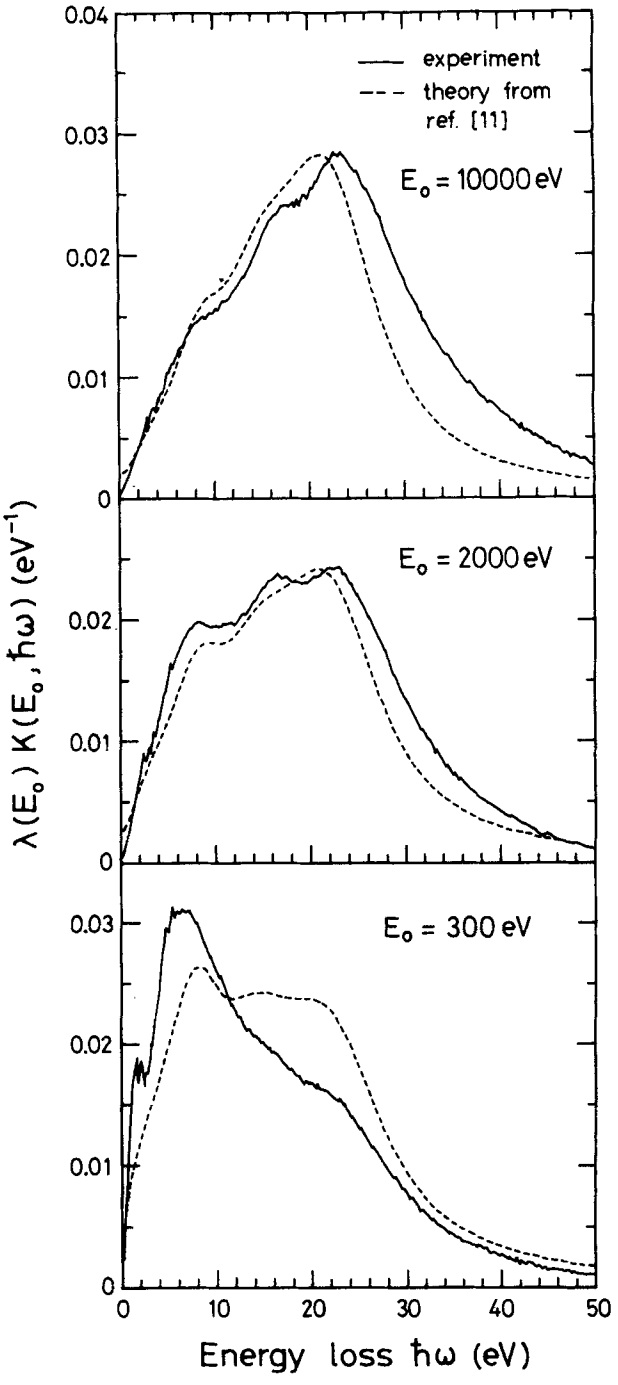

Figure 4. $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ in Fe calculated by the model in Ref. 11 at 300, 2000 and 10 000 eV primary electron energy (dashed lines) and $\lambda(E_0) \cdot K(E_0, \hbar\omega)$ determined from experimental REELS (solid lines). Note that the two sets of curves should be compared on an absolute scale and that no adjustable parameters were used in the theoretical calculations.

It is expected that this formalism will, in the future, increase the quantitative information that can be extracted from REELS experiments.

CONCLUSION

It was shown that a simple model which considers the inelastic electron scattering cross-sections from REELS experiments to consist of a pure surface and a pure bulk

component is insufficient for a quantitative description. It was also shown that a more realistic model which takes into account the physical conditions in a REELS experiment can reproduce the experiments quantitatively.

Acknowledgement

Financial support from The Danish Research Academy, the Spanish Ministry of Education and Science and The Danish Natural Science Research Foundation is acknowledged.

REFERENCES

1. J. C. Ingram, K. W. Nebesny and J. E. Pemberton, *Appl. Surf. Sci.* **44**, 279 (1990).
2. Y. Ohno, *Phys. Rev. B* **39**, 8209 (1989).
3. G. Chiarello, E. Colavita, M. De Crescenzi and S. Nannarone, *Phys. Rev. B* **29**, 4878 (1984).
4. F. Yubero, J. M. Sanz, E. Elizalde and L. Galán, *Surf. Sci.* **237**, 173 (1990).
5. S. Tougaard and J. Kraaer, *Phys. Rev. B* **43**, 1651 (1990).
6. S. Tougaard, *J. Electron Spectrosc.* **52**, 243 (1990).
7. J. Lindhard, *K. Dan. Vidensk. Mat.-Fys. Medd*, **28**(8), (1954).
8. R. H. Ritchie, *Phys. Rev.* **106**, 874 (1957).
9. S. Tougaard and I. Chorkendorff, *Phys. Rev. B* **35**, 6570 (1987).
10. J. Daniels, C. v. Festenberg, H. Raether and K. Zeppenfeld, *Springer Tracts Mod. Phys.* **54** (1970).
11. F. Yubero and S. Tougaard, *Phys. Rev. B* in press.
12. J. H. Weaver, C. Krafka, D. W. Lynch and E. E. Koch, *Physics Data, Optical Properties of Metals*, No. 18. Fachinformationszentrum Energie, Physik, Matematik GmbH, Karlsuhe (1981).
13. S. Tanuma, C. J. Powell and D. R. Penn, *Surf. Interface Anal.* **17**, 911 (1991).