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Retrieving the dielectric function of diamond from valence electron energy-loss spectroscopy

L. Zhang,[1,*] R. Erni,[2] J. Verbeeck,[1] and G. Van Tendeloo[1]
[1]*EMAT, University of Antwerp, Groenenborgerlaan 171, B2020 Antwerp, Belgium*
[2]*National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720, USA*

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A data-acquisition and data-processing method is proposed that aims at minimizing the effect of retardation on the Kramers–Kronig analysis of valence electron energy-loss spectra. This method is applied to diamond, which, due to its high dielectric constant, is a material that shows strong retardation effects and thus is a challenging material to be studied by valence electron energy-loss spectroscopy. The results obtained show a significant improvement but still show small discrepancies with respect to optical data, which are most likely due to the residual retardation contributions and the fact that nonzero momentum transfers are measured.

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I. INTRODUCTION

Both bulk diamond and diamond thin films widely attract scientific interest because of their outstanding mechanical, electronic, and optical properties. For example, there is the wide transparent range from UV to the far infrared connected with the large band gap of ~5.45 eV, the high thermal conductivity, and the high electron emission efficiency. These properties are promising for a wide area of applications such as optical component coatings, electrochemical electrodes, microelectromechanical systems (MEMS), and electron emitting surfaces for flat-panel displays.[1–3] All these properties are mainly determined by the specific band structure of diamonds that can be tailored by, e.g., changing grain size or adding dopants.[4]

Valence electron energy-loss spectroscopy (VEELS) carried out in a scanning transmission electron microscope (STEM) is an experimental technique able to provide detailed band structure information on the nanoscale. By performing a Kramers-Kronig analysis (KKA), the dielectric function can be derived from VEELS spectra.[5] The main advantage of VEELS compared to optical techniques such as vacuum ultraviolet spectroscopy is its high spatial resolution.

In this contribution, VEELS with high energy resolution and high spatial resolution is applied to a bulk diamond rather than to a nanodiamond. Even though for a bulk diamond a high spatial resolution is not required, it allows for directly comparing the VEELS data to the optical data.[6] KKA analysis of VEELS spectra has been successfully applied on various materials for years but for materials of high dielectric constants, it is hard to apply the technique directly. This is because when a fast electron penetrates a sample, it will suffer from retardation effects. The speed of light in a material is given by $c' = c/\sqrt{\varepsilon_1(E)}$, where c is the speed of light in vacuum and ε_1 is the real part of the dielectric constant of the material. In a material with a high dielectric constant, the incoming electrons may be faster than the speed of light in the material and thus suffer from retardation losses.[7] The higher the dielectric constant is, the higher the probability of the retardation losses is and thus the more retardation radiation will be generated. So, the spectral analysis of materials with a high dielectric constant, e.g., diamond, requires several steps such as zero-loss subtraction, correction for multiple scattering, correction for relativistic effects, and KKA. To verify the reliability of our analysis, the final outputs will be compared to the optical data from the literature.[6]

II. THEORY

Electron energy-loss spectra can be divided in three main regions, the zero-loss peak (ZLP) containing elastically and quasi-elastically scattered electrons, the valence-loss region including the plasmon peak, and the core-loss region containing element-specific absorption edges, which are due to the excitation of inner shell electrons. The valence-loss region of the spectra reflects the excitation of individual valence electrons from the ground state to the conduction bands. VEELS, thus, contains information about the band structure encoded in the joint density of states of the material.[5]

A. Kramers-Kronig analysis

VEELS is commonly treated in the dielectric formalism. For the case in which only single scattering is considered, the relation between the energy loss $S(E)$ and the complex dielectric function $\varepsilon(E)$ can be written as[5]

$$S(E) = \frac{2I_0 t}{\pi a_0 m_0 v^2} \mathrm{Im}\left[\frac{-1}{\varepsilon(E)}\right] \ln\left[1 + \left(\frac{\beta}{\theta_E}\right)^2\right], \tag{1}$$

where I_0 is the integral intensity of the ZLP, t is the thickness of the sample, v is the speed of incident electrons, β is the collection semi-angle, and $\theta_E = E/\gamma m_0 v^2$ is the characteristic scattering angle.[5] Since the relation between $S(E)$ and $\varepsilon(E)$ is obtained by the energy-loss function, the dielectric function can be derived by KKA as follows:[5]

$$\mathrm{Im}\left[\frac{-1}{\varepsilon(E)}\right] = \frac{S(E)\pi a_0 m_0 v^2}{2I_0 t} \cdot \frac{1}{\ln\left[1 + \left(\frac{2\beta E_0}{E}\right)^2\right]}, \tag{2}$$

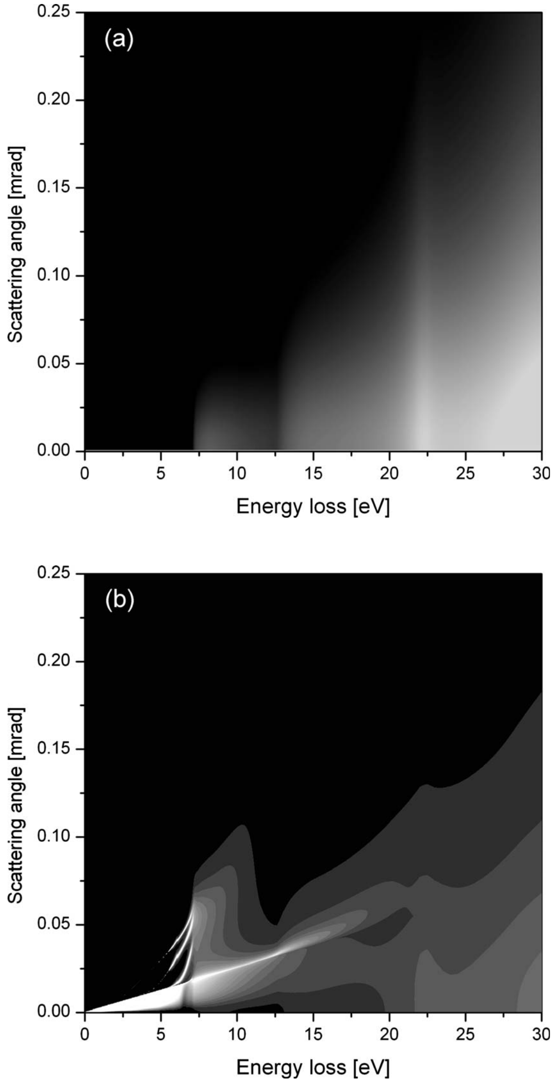

FIG. 1. Calculated single scattering probability of diamond. (a) contains only volume excitation; (b) contains volume excitation, surface loss, and retardation effect. The intensity is proportional to the double differential cross section for a given energy loss and scattering angle.

$$\mathrm{Re}\left[\frac{1}{\varepsilon(E)}\right] = 1 - \frac{2}{\pi}P\int_0^\infty \mathrm{Im}\left[\frac{-1}{\varepsilon(E)}\right]\frac{E'dE'}{E'^2 - E^2}. \quad (3)$$

Here, E_0 is the energy of the incident electron. Thus, the dielectric function can be obtained as

$$\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E) = \frac{\mathrm{Re}\left[\frac{1}{\varepsilon(E)}\right] + i\,\mathrm{Im}\left[\frac{-1}{\varepsilon(E)}\right]}{\left\{\mathrm{Re}\left[\frac{1}{\varepsilon(E)}\right]\right\}^2 + \left\{i\,\mathrm{Im}\left[\frac{-1}{\varepsilon(E)}\right]\right\}^2}. \quad (4)$$

Instead of getting the dielectric function straightforwardly as shown above, in real experimental conditions, the energy-loss spectrum is affected by signals such as surface losses, multiple scattering effects, and retardation contributions (guided light modes, Cerenkov losses). Hence, before performing a KKA, the experimental energy-loss spectrum needs to be corrected for such contributions.

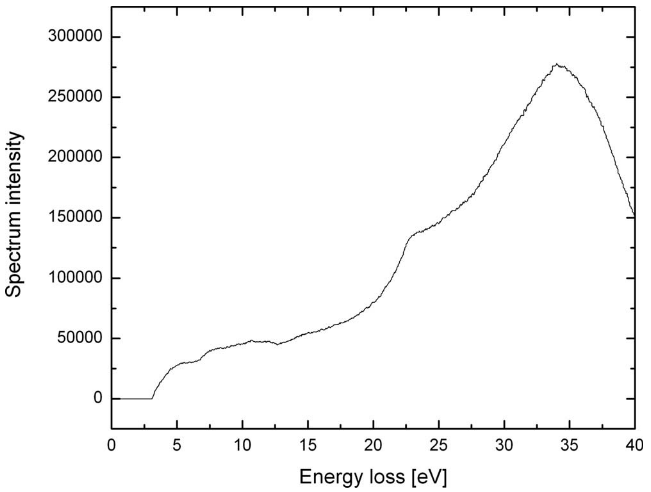

FIG. 2. A nanodiamond film VEELS spectrum with ZLP subtracted by Gaussian and Lorentzian fitting.

B. Multiple scattering correction

In very thin samples, it is safe to assume that all of the incoming electrons are scattered (inelastically) only once; the probability of more than one scattering event within the sample is negligible.[5] However, in thicker samples, this assumption no longer holds; electrons can be scattered more than once. Multiple scattering has a severe impact on the VEELS spectra. Therefore, the contributions induced by multiple scattering have to be removed. $S(E)$ can be derived by a Fourier-log deconvolution[5]

$$s(v) = z(v)\ln\left[\frac{j(v)}{z(v)}\right], \quad (5)$$

where $j(v)$ and $z(v)$ are the Fourier transform of the recorded VEELS data and ZLP.

C. Surface-loss correction

Under the assumption that the surface-loss contribution is independent of the thickness of the sample and the bulk loss is assumed to linearly increase with the thickness, Mkhoyan *et al.*[8] derived the following expression to describe the total spectral intensity I_0 consisting of the bulk contribution I_b and the surface contribution I_S:

$$I_0'(E,t) = I_b + \frac{1}{t}I_s(E). \quad (6)$$

This assumption only holds for experiments with a finite thickness. According to Eq. (6), if two spectra of different thicknesses t_i and t_j are known, the surface-loss contribution from Ref. 8 becomes

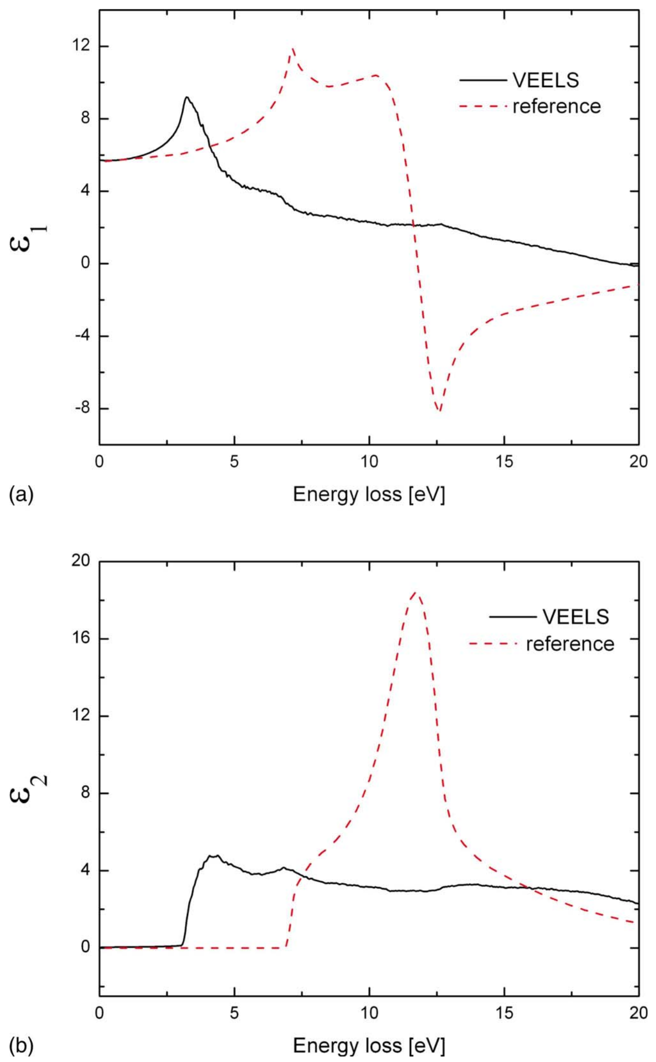

FIG. 3. (Color online) The black solid lines in (a) and (b) show the dielectric function ε_1 and ε_2 calculated from uncorrected spectra, respectively. The dark gray (red) dashed line is the reference dielectric function.

$$I_s(E) = \left(\frac{t_i t_j}{t_j - t_i}\right)[I'_0(E,t_i) - I'_0(E,t_j)]. \tag{7}$$

Equation (6) is based on the assumption that the surface-loss contribution is independent of the thickness of the sample and the bulk loss is linear with the thickness of the sample, so the more accurate the thickness measurement is, the more accurate the surface losses estimation can be. For thin films, however, it has to be expected that the excitations of the upper and the lower surfaces are coupled and that the surface-loss contribution is thus thickness dependent. In Ref. 8, Mkhoyan *et al.*, however, showed that Eq. (6) is a good approximation that can be applied to significantly suppress surface contributions in VEELS spectra.

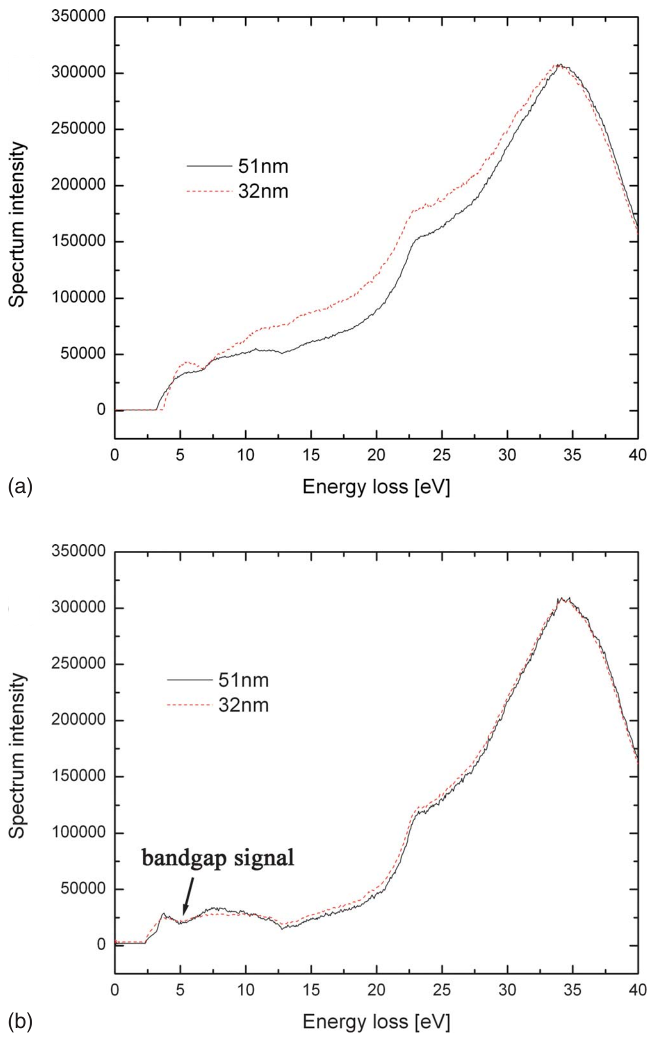

FIG. 4. (Color online) (a) shows two spectra with different thicknesses before surface-loss correction; (b) shows the same two spectra after surface-loss correction. The black solid line is ~50 nm thick and the dark gray (red) dashed line is ~30 nm. (These thickness values should be mentioned in the experimental part.)

D. Retardation-loss correction

Figure 1 shows a calculation of the scattering probability of diamond (100 nm, 300 kV) using the Kröger formula.[7,9] An example of using the Kröger formula with dielectric data from optical experiments[6] is given in Fig. 1(a), which considers only volume losses, and Fig. 1(b), which includes surface and retardation losses. This illustrates that surface losses and retardation effects lead to a pronounced scattering intensity at small angles (<0.1 mrad) in the energy loss range from 0 to about 8 eV. At scattering angles exceeding 0.1 mrad, Figs. 1(a) and 1(b) are however very similar. This means that the undisturbed bulk dielectric information can be obtained if the scattering intensity at small angles is suppressed. This fact can be exploited in experiments by either blocking the central part of scattering intensity[10] or by collecting two spectra at different collection angles.[11] We adopt the last strategy by acquiring two spectra with different camera lengths in combination with a fixed spectrometer entrance aperture. Subtracting these spectra will lead to a spectrum with reduced retardation and surface effects. It has to be noted however that now the spectrum is related to the loss

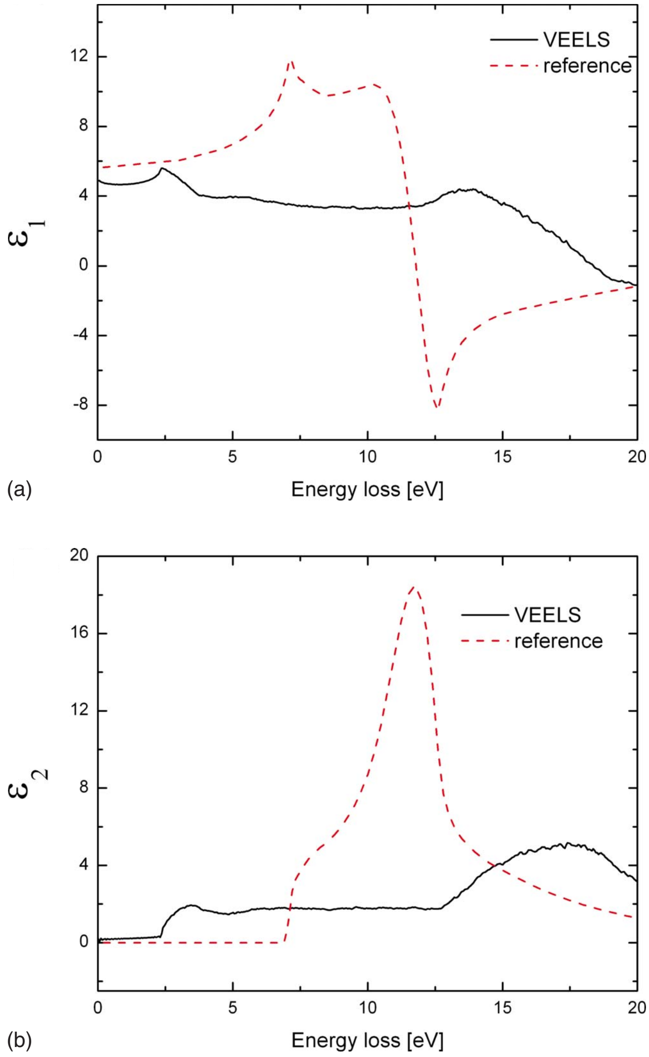

FIG. 5. (Color online) The black solid lines in (a) and (b) show the dielectric function ε_1 and ε_2 calculated from surface and multiple scattering correction spectra, respectively. The dark gray (red) dashed line is the reference dielectric function. Still, the agreement is far from being satisfactory.

function for momentum transfers $q \neq 0$ integrated in a ring. This will give different results as compared to optical measurements at $q=0$.

III. EXPERIMENT

The epitaxial grown bulk diamond sample is prepared by chemical vapor deposition (CVD). In order to obtain a suitable transmission electron microscope (TEM) sample, the bulk diamond is first cut into a thin foil by a laser, which is further thinned by argon ion milling.

VEELS spectra of the diamond film used in Figs. 2 and 4 are recorded for two different thicknesses of approximately 30 and 50 nm to be able to correct for surface effects. The spectra were recorded by using a transmission electron microscope equipped with an illumination Cs corrector and a Wien-filter type electron monochromator (FEI Titan 80-300; Ernst-Ruska Center, Forschungszentrum Jülich, Germany).

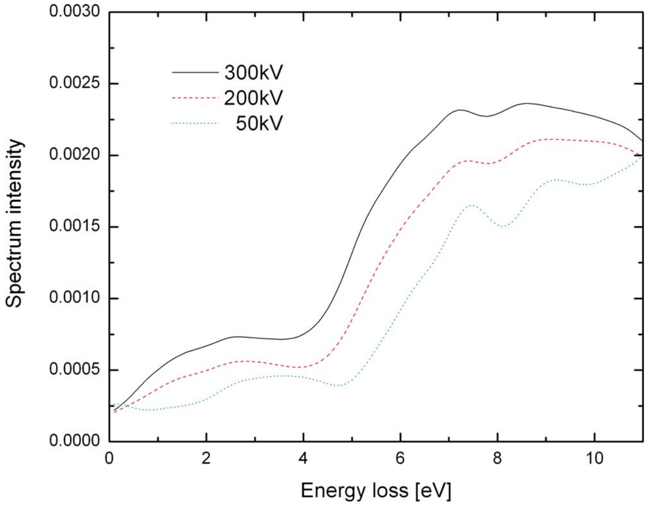

FIG. 6. (Color online) Spectra calculated from the reference dielectric function for different acceleration voltages. The differences in the spectra show the effects of retardation on the spectral shape which is especially important for energies below 10 eV.

The energy resolution was set to 200 meV when operating at 300 kV with a spatial resolution less than 0.2 nm. The probe semiconvergence and the effective collection angle is ~25 mrad. Fifty spectra were acquired for each position on the sample with an acquisition time of 0.1 s. The 50 spectra were first aligned with respect to the ZLPs and then added in order to increase the signal to noise ratio.

A second data set was recorded on a Philips CM30 without a monochromator and an energy resolution of ~0.6 eV at two different collection angles, 0.09 and 2.08 mrad. This data set is used in Fig. 7 to correct for surface and retardation effects.

IV. RESULTS

The first data set recorded at two different thicknesses is treated in different steps. First, the ZLP is removed by fitting a Gaussian and a Lorentzian peak, making use of the fact that the monochromated spectra show a nearly symmetric peak shape.[12] The spectra are extended with a power law fit to 1000 eV, which is required for the KKA procedure. The result is shown in Fig. 2. Applying a KKA transformation on these data leads to Fig. 3. The obtained dielectric function is still quite different from the optical data,[6] so clearly, further treatment is necessary.

A. Removal of multiple scattering and surface effects

In the second step, we remove multiple scattering by Eq. (5) and then apply Eqs. (6) and (7) to remove the surface losses by subtracting the two spectra taken at different thicknesses. Figure 4 shows the resulting loss function. This function is again extended to 1 000 eV by using a power law fit and the KKA transformation leads to a new estimate of the dielectric function shown in Fig. 5. The comparison to the optical data is still far from satisfactory, indicating that retardation effects play an important role.

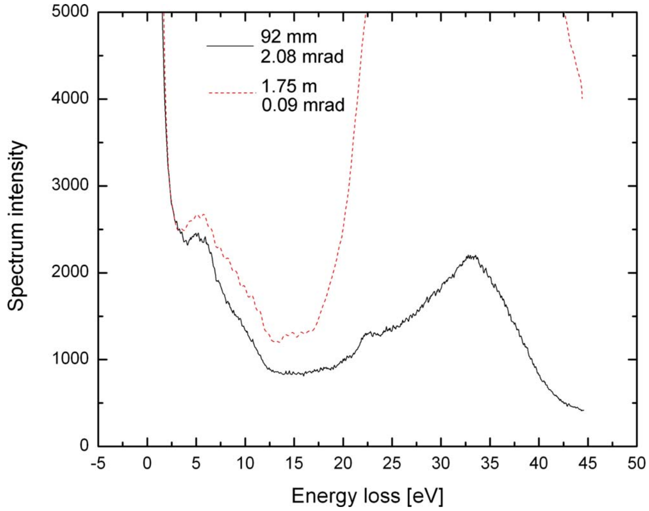

FIG. 7. (Color online) Two spectra recorded with two different camera lengths with corresponding collection angles 0.385 mrad and 0.028 mrad. Normalized to ZLP.

B. Elimination of the retardation effect

Figure 6 shows a series of spectra calculated from the dielectric function by the Kröger formula[9] for different accelerating voltages in the TEM. It clearly shows that retardation losses are present. Although we can decrease the accelerating voltage to minimize the retardation losses, for diamond, the maximum ε_1 is ~ 11 at an energy loss ~ 11 eV [shown in Fig. 3(a), reference curve], indicating that the accelerating voltage should be down to 30 kV to fully suppress retardation losses.

Therefore, we acquired a second data set with two spectra with different collection angles as shown in Fig. 7. In order to normalize the spectra to the ZLP, it is necessary that we collect the whole central beam in the entrance aperture of the spectrometer. If this situation is fulfilled, we can normalize the two spectra to the ZLP and subtract them from each other, leading to a spectrum containing a scattering in a ringlike range of scattering angle between 0.09 and 2.08 mrad, as shown in Fig. 8. Again, the spectrum is deconvolved for multiple scattering and extended to 1000 eV. Applying KKA leads to Fig. 9. Clearly, the result is much more satisfactory now, showing the importance of retardation removal.

V. DISCUSSION

Figures 3, 5, and 9 show that after a series of corrections, the output dielectric functions are similar to the reference dielectric function. This indicates that multiple scatterings, surface losses, and retardation effects all have an important effect on the spectrum when doing KKA. The big differences between Figs. 5 and 9 indicate that a retardation-loss correction is an important and necessary step to reach agreement with the calculated spectrum and the reference (optical) data.

After the series of corrections is applied, the result of the KKA is strongly improved, i.e., the dielectric function derived from VEELS matches, in its major characteristics, the optical dielectric function; see Fig. 9. However, there are still

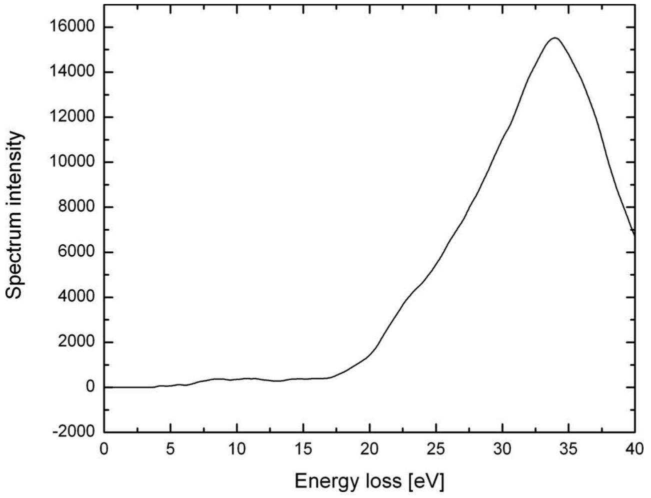

FIG. 8. Single scattering signal subtracted from the spectra with two different collection angles.

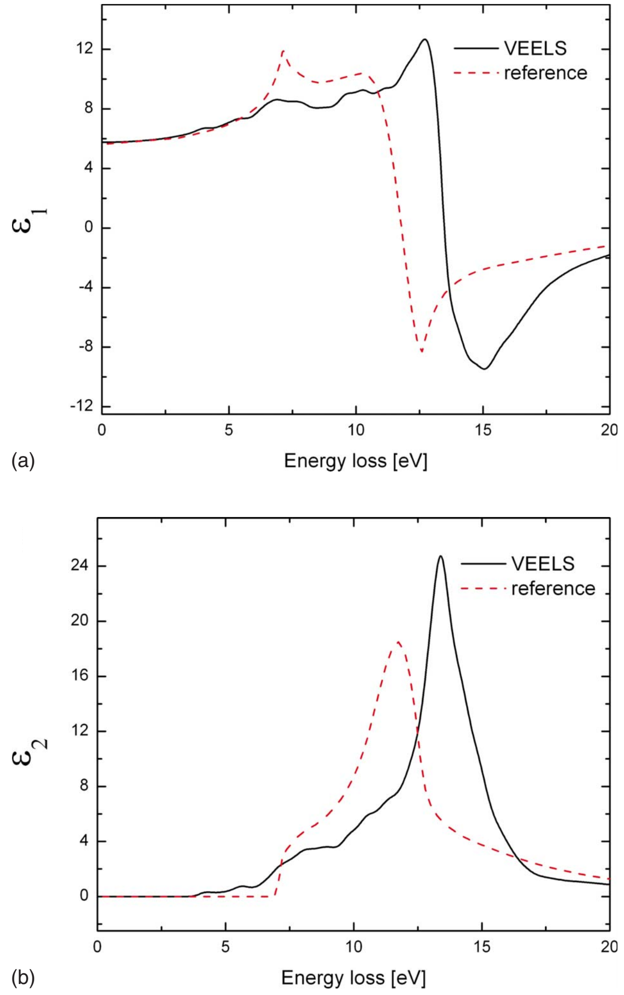

FIG. 9. (Color online) The black solid lines in (a) and (b) show the dielectric function ε_1 and ε_2 calculated from surface loss, multiple scattering, and retardation loss correction spectra. The dark gray (red) dashed line is the reference dielectric function. The agreement improved.

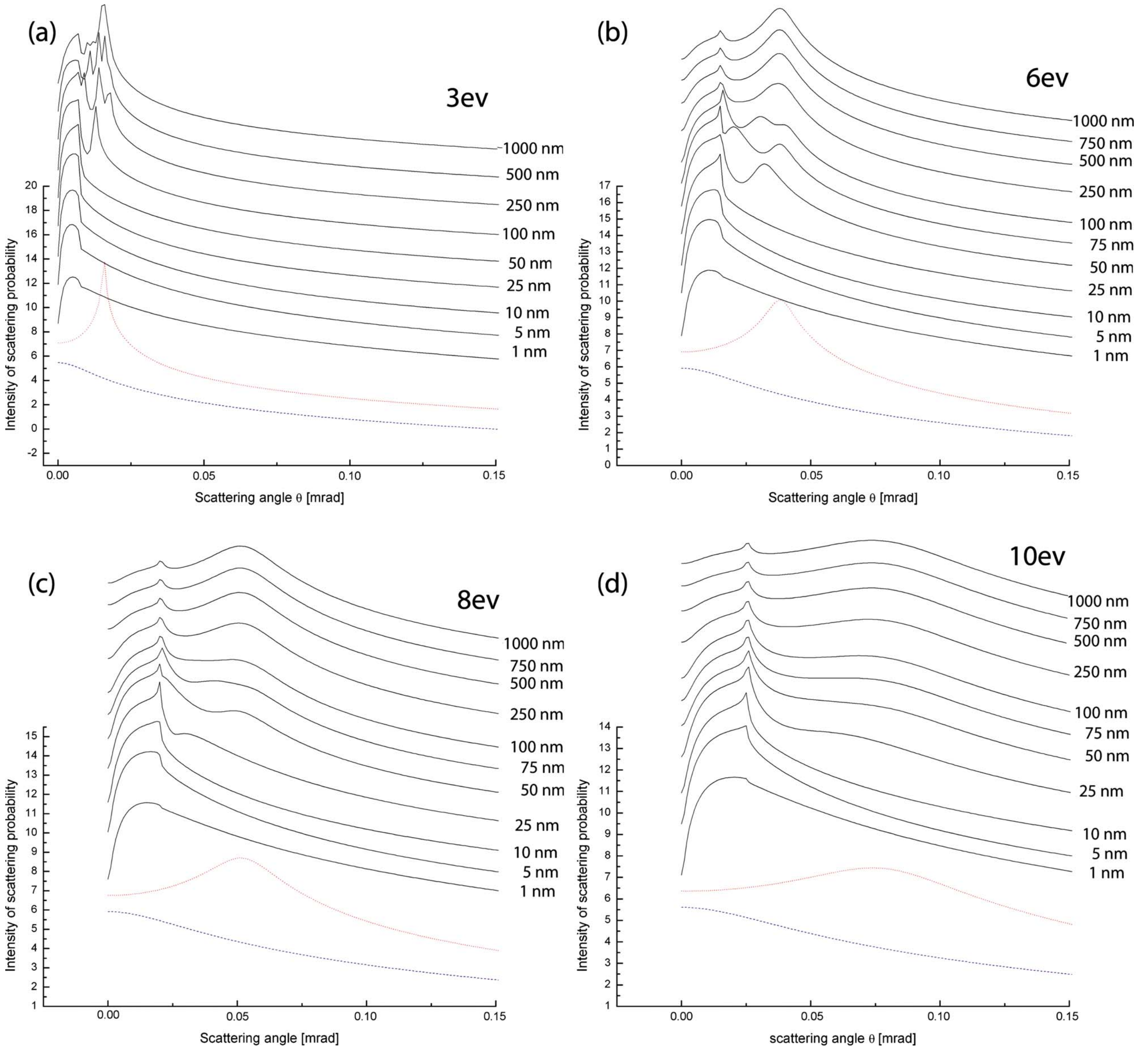

FIG. 10. (Color online) The calculated scattering probability of the diamond samples in different thicknesses at a certain energy loss. There is a 70% offset on the *y* axis.

shifts of peak positions observable and also a certain loss of details. One major reason is that the method which is used to suppress the impact of retardation contributions neglects the effects that arise from combined inelastic-elastic scattering. Varying the collection angle in order to measure the retardation contribution is based on the assumption that the low-angle inelastic scattering, containing the retardation contribution, is only found at small collection angles. However, through combined inelastic-elastic scattering, the low-angle inelastic scattering is transferred to any diffraction spot. By increasing the physical collection angle, the relative contribution of the retardation effect of the forward scattered beam is suppressed. However, additional retardation effects become part of the detected signal as additional diffraction spots fall into the collection aperture. Hence, the method of varying collection angles presented here can be used to reduce the impact of retardation effects but because of the combined inelastic-elastic scattering, the method cannot fully suppress it. This is particularly true for the case of crystalline materials where, with varying collection angles, different amounts of diffraction spots fall into the collection aperture. This can be optimized by choosing proper values of collection angles. Another likely reason is that the different momentum transfers are present in the EELS experiment as opposed to the optical results. Using the retardation removal step leads to a dielectric function averaged over the ringlike detector as opposed to the optical dielectric function at $q=0$. This will be investigated in detail in future work. Other sources of discrepancy are the effect of noise and finite energy resolution and how this is transmitted to the correction procedures and the KKA step. Numerical work is being carried out to investigate this in detail.

Sample thickness effects could also still play a role since the estimate of the thickness is not necessarily very accurate and the assumption that the surface losses linearly vary with thickness might not hold for very thin samples where the surface modes could become coupled.

In addition to this rather general data analysis technique proposed above that can be used to suppress retardation effects, we would like to point out that there is a simple alternate method to minimize retardation effects. Figure 10 shows the calculated scattering probabilities for a diamond sample at different thicknesses but for given energy losses. Figures 10(a)–10(d) are the scattering probabilities at 4, 5, 6, and 7 eV, respectively. In each figure, the dashed line is the scattering probability of the volume loss, the dotted line is the scattering probability of the volume loss plus retardation effect, and the solid lines are the scattering probabilities of volume loss, surface loss, and retardation effect. Figure 10(a) shows that the retardation peaks start to appear at a thickness of ~50 nm for an energy loss of 3 eV. This critical thickness in Figs. 10(b)–10(d) decreases to ~25 nm for energy loss of 6, 8, and 10 eV. This indicates that for diamond films thinner than ~25 nm, retardation effects are expected to be small. However, for such thin films, the surface contribution needs to be properly considered before the actual bulk dielectric information can be derived.

VI. CONCLUSION

We applied a set of corrections in obtaining the dielectric function for diamond from VEELS experiments. The best results are obtained from spectra recorded at two different collection angles that were shown to greatly reduce retardation effects. Although, due to its high dielectric function, diamond is a difficult material for a VEELS study, i.e., the impact of retardation effects is large, the VEELS result is close to the reference. The obtained dielectric function still shows deviations from the optical result, which is most likely due to the residual retardation contributions and nonzero momentum transfers.

VII. ACKNOWLEDGMENTS

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*Corresponding author. FAX: +32(0)32653257; liang.zhang@ua.ac.be

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