Analysis of VEEL spectra of diamond using a dedicated STEM: isolation of Čerenkov loss contributions

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Abstract. The analysis of multiple EEL (electron energy-loss) spectra often requires normalisation of data to eliminate, for example, relative variations in thickness. In this case, data would only be reliable if it were normalised to a region in the spectrum, where the intensity varied with thickness alone. This raises the question of where an appropriate region is located, from which to extract the normalisation constants. The introduction of structure into the spectrum at certain thicknesses, such as energy lost via Čerenkov radiation emission, are clear regions to avoid. Identifying energy-loss contributions in the valence band region will provide further clarification for this process.

1. Introduction
One particular area of valence electron energy-loss spectroscopy (VEELS) that has benefitted from recent increases in energy resolution is the accuracy in the determination of the bandgap. However, direct analysis is still limited by the presence of relativistic contributions in the form of Čerenkov losses. Initial studies into the Čerenkov contribution to diamond EEL spectra identify a clear peak that increases in intensity as the sample thickness increases [1]. For diamond, this peak occurs within the 8-12 eV energy loss regime. Recent publications have shown that the presence of Čerenkov structure in VEEL spectra of many semiconductor materials, demonstrates the bandgap cannot be determined by direct inspection [2]. Figure 1 shows the rise in the 6-12 eV region of spectra often seen in data recorded at thicker regions of the sample.

![Figure 1](image_url)

Figure 1. VEEL spectra of colourless natural diamond. The ZLP was removed by applying a power-law model to the high energy tail and extracting the residual signal. The change in spectral shape can be clearly seen at increasing thickness. The thickness calculations are made using the log-ratio method described in Egerton [3].

We show that the spectral change, like that highlighted in figure 1, is primarily due to interband transitions, and not due to the onset of a Čerenkov peak. Results in the present contribution show the
non-relativistic spectral features, corresponding to interband transitions, vary in intensity once the relativistic Čerenkov contributions are excluded.

2. Methodology

The diamond sample was produced via the CVD (chemical vapour deposition) process. The diamond was brown in colour [4] and composed of a single crystal. To produce an ‘electron transparent’ sample, suitable for EEL study at well defined thickness, part of the sample was thinned using an FEI Focused Ion Beam system (see figure 2). The ion beam was directed onto the edge of the sample in order to form a ‘wedge’ of increasing thickness. No tilts were required as the FIB system had an inherent tilt of ≈ 1°, resulting in an adequate penetration depth of ≈ 10 μm. The FIB was operated with a beam current of 300 pA.

The spectra were acquired using a VG HB-601 STEM (scanning transmission electron microscope). The spectrometer system was a Gatan Enfina instrument, enabling the acquisition of a spectrum image. The system operates with a HT voltage of 100 kV, has an energy resolution of 0.35 eV (FWHM of the ZLP) and is capable of high dispersion (0.01 eV per channel). These factors enable detailed scrutiny of the valence band spectra and in particular, the interband transitions.

An objective aperture of 21.3 mrad was applied to limit the effect of spherical aberrations and provide good imaging conditions. To gain high quality spectral statistics, whilst enabling the displacement of the collector aperture to selectively exclude different k-space contributions, a collector aperture of 1.34 mrad was used. This also prevented saturation of the detector provided an appropriate acquisition time was used.

3. Results and Discussion

Several methods for the removal of relativistic contributions from the spectrum have been described in detail by Stöger-Pollach and Schattschneider [5]. The fundamental principle of one of these methods is to use the collector aperture or objective aperture in a TEM, to exclude Čerenkov losses in the scattering distribution of the diffraction plane. A comparable method demonstrated in this contribution, is to physically displace the collector aperture beyond the inelastic Čerenkov scattering angle. Čerenkov radiation is emitted whenever an electrically charged particle passes through a dielectric material at a speed exceeding the speed of light in the material. Atoms in the material are excited as the charged particle passes through, and so they emit a coherent wavefront of radiation. The charged particles will lose energy in the process. For Čerenkov emission to occur, the condition expressed in equation 1 must be valid,

$$\varepsilon(\omega) \frac{v^2}{c^2} > 1$$  \hspace{1cm} (1)

$\varepsilon(\omega)$ represents the relative permittivity of the medium, $v$ is the speed of the incoming charged particle and $c$ is the speed of light in the material. If this condition is not met, then no wavefront will be formed. A diamond sample probed with 100 kV electrons satisfies the condition in equation 1. The characteristic electron scattering angle is given by equation 2,

$$\theta = \frac{1}{k^2} \left( \frac{\varepsilon \omega^2}{c^2} - \frac{\omega^2}{v^2} \right)^{1/2}$$  \hspace{1cm} (2)
Under the same 100 kV operating system, for electrons with approximately 10 eV energy losses, the inelastic scattering angle for Čerenkov losses is 0.6 mrad. It would therefore be possible to exclude the Čerenkov contribution from the spectrometer, by displacing the collector aperture beyond 0.6 mrad from the optical axis.

Three spectra are displayed in figure 3A. One spectrum was recorded with the collector aperture centred on the through beam, whilst the other two spectra were recorded with the aperture displaced by approximately 1.34 mrad. Although weaker in terms of statistical data, the rise in relative counts between 6.5 and 12.5 eV, characterized by a ‘dip’ at approximately 12.5 eV, is clearly visible. The dip is even more pronounced in the displaced aperture spectra. If Čerenkov losses were accountable for the rise, one would expect the opposite.

Figure 3. (A) VEELS spectra of CVD diamond, recorded with the collector aperture positioned at three different locations. The displaced aperture A and B spectra are shifted vertically by 150 and 300 counts, respectively, for clarification. Each spectrum was recorded at a thickness of 1.1 inelastic mean free path lengths, to ensure identifiable spectral change. Low loss intensity at letters (a) to (d) corresponds to transitions at the same letters in figure 4. (B) VEELS spectra of CVD diamond showing the damping of the surface and bulk plasmons at higher scattering angles.

With reference to figure 4, we suggest the following explanation for the spectral change identified in thicker regions of the sample. When a passing electron excites a valence band electron into the conduction band, energy and momentum must be conserved. In thin regions of the sample (<0.3 inelastic mean free path lengths), directing attention to the Γ point (k=0), the vertical direct transitions at (a) and (b), denoting the bottom of the 1st and 2nd conduction band, are more likely to occur. The majority of the beam electrons do not have adequate momenta to promote the indirect transitions (c) and (d). Moving to thicker regions in the sample, this condition changes as a greater number of beam electrons are scattered to higher angles. Competing channels for valence band electrons, e.g., to undergo indirect transitions and filling states at the slopes of the conduction band, are opened and events such as (c) and (d), boosting the loss intensity at around 8 eV in figure 1, can be detected now. The density of states is greatest at the minima of the conduction band. As such, the majority of transitions occur at these regions. The ‘dip’ between 10 and 12 eV, clearly identifiable in the spectra in figure 1, is a result of the regions of low state density. This illustrates that the diamond EELS spectrum in the 6-16 eV region is representative of the dispersion surface of the band structure.
Figure 4. Diamond band structure diagram calculated by an \textit{ab intio} LCAO (linear combination of atomic orbitals) method \cite{6}. The colourless natural diamond EEL spectrum identifies the corresponding band structure transitions. This spectrum was recorded at 0.4 inelastic mean free paths using with the surface and bulk plasmon extracted using a Gaussian model. The letters (a) – (d) denote transitions corresponding to the low loss intensity at the same letters in figure 3.

It is important to recognise that Stöger-Pollach and Schattschneider do not support this method being undertaken on a STEM. Their argument is based on the principle that the scattering distribution is different for a convergent beam probe, than that of the parallel illumination in normal TEM operation. Whilst we do not disagree that this is the case for a wide convergence beam, in reality, it is possible to achieve narrow convergence by using a small objective aperture. This is supported by the displaced aperture spectra (see figure 3B), where a relative drop in the intensity for the surface plasmon (22 eV) and bulk Plasmon (32 eV) can be clearly identified. It has been previously reported that the surface and bulk plasmon intensities have a $1/\theta^2$ and a $1/\theta^3$ scattering distribution relationship respectively \cite{7}. This data suggests that the resulting diffraction plane retains an angular scattering distribution similar to that produced in a conventional TEM.

4. Conclusion
In conclusion, the results and explanation presented here, show that the spectral changes in the 6 to 12 eV region, previously identified as the onset of a Čerenkov feature, are primarily due to the increase in contributions of the indirect interband excitations. For a more complete analysis, future research will aim to identify and isolate the Čerenkov peak from experimentally obtained spectra. This will aid understanding of how Čerenkov losses contribute to the overall spectral appearance.

References
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