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Theory for High Energy Resolution EELS of Vibrational and Defect States

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The development of monochromators coupled to spectrometers capable of energy resolution better than 10 meV has made it possible to do visible and infrared spectroscopy in the electron microscope. In some ways the theory required to quantify the recorded signals is similar to what has been used for the low loss (equivalent to UV in photon spectroscopy) part of the spectrum. Calculations of the dynamical matrix, frequently using the techniques of density function theory, are required to describe vibrational modes

The characteristic scattering angles are much smaller than are typical for low loss studies. For energy losses typical of optical excitations characteristic angles are between 10 and 20 μrads, for vibrational losses they range from 0.3-3 μrads. For many purposes one can neglect any change in direction and describe the electron beam as a point charge moving at constant velocity $\delta(\mathbf{r}\text{-}\mathbf{v}t)$ [1]. The energy loss, ΔE, can be calculated from the work done by the electric field induced by the beam sample interaction $\Delta E = -e\int E^{ind}\left(\mathbf{r}_e,t\right)\mathrm{d}\mathbf{r}_e$ along the trajectory followed by the beam electron. The induced electric field is calculated form the scalar and vector potentials and the boundary conditions applicable to the particular geometry [2]. The response of the material is described by the frequency dependent dielectric function. Given the relatively poor energy resolution compared to Raman and IR spectroscopy it is acceptable to use simple models for the dielectric response such as the Drude model for metals and the damped oscillator for insulators. For vibrational modes the response is greatest when it involves polar materials, such as oxides. From Fig 1 it can be seen that the real part ranges from -3 to +8 for SiO_2. When the speed of the fast electron exceeds the speed of light in a material, $\frac{c}{\sqrt{\varepsilon_r}}$, Cerenkov radiation is emitted, and a relativistic theory should be used. In other cases it is quite acceptable to use a non-relativistic theory where the magnetic fields generated by the moving fast electron are neglected.

A consequence of the small scattering angles is "delocalization", the range over which the signal extends in real space from a sharp feature such as an atomically flat interface or a transition at an atomic site. This can range from 10's of nm for optical excitations to more than 100 nm for vibrational modes [3]. In the simplest theory with an infinite range of collection angles the variation in real space can be described by a K_0 Bessel function. Unfortunately this goes to infinity at the position of an interface. Restricting the integration range to a finite convergence angle gives a well-behaved response function. The simple theory also assumes that the specimen is infinite in the beam direction. For vibrational losses the "delocalization" is greater than the specimen thickness. Applying appropriate boundary conditions gives coupled modes at top and bottom surfaces of which the symmetric is the most important.

To achieve nanometer or atomic spatial resolution it is necessary to suppress and avoid the scattering from oscillating dipoles and form a signal from the weaker impact scattering. One way of doing this is to use a spectrometer entrance aperture displaced (even slightly) from the probe forming objective aperture [4]. It is then necessary to use a microscopic theory for phonon excitation. Scattering wave vectors are

predominantly perpendicular to the beam direction in the plane of the specimen, limited by the combination of the probe angle and the collection angle. The signal is dominated by parts of the Brillouin zone where the relevant phonon frequency does not change much with wavevector [4]. It is then necessary to do a 2D calculation of phonon modes such as shown in Fig 3 to identify the relevant parts of the Brillouin Zone. Since the probe will span more than one Brillouin Zone, as shown in Fig. 2, if atomic resolution is desired it is also necessary to consider Umklapp processes and elastic dynamical diffraction both before and after the phonon scattering event.

References:

[1] D Jackson in "Classical Electrodynamics", (Wiley, New York).
[2] J Garcia de Abajo, Rev. Mod. Phys. **82** (2010), p. 109.
[3] OL Krivanek et al., Nature **514** (2014), p. 209.
[4] C Dwyer, Phys. Rev. **B96** (2017), art. 224102.

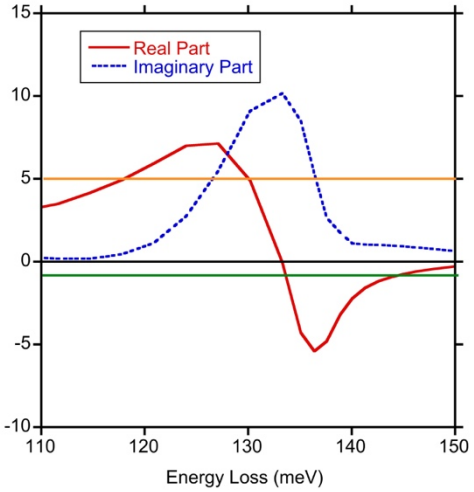

Figure 1. Real and imaginary parts of the dielectric function for silica. Note that the real part exceeds the threshold for Cerenkov radiation for 60 kV from 120 to 130 meV (orange line) and is below 1 (green line) from 132 meV to 142 meV

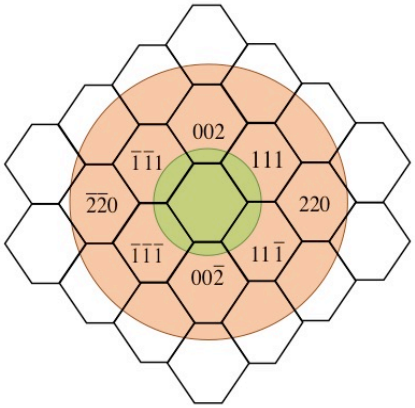

Figure 2. Section of [110] zone for Si. The orange circle shows a 28 mrad objective aperture. The green circle a 13 mrad detector aperture

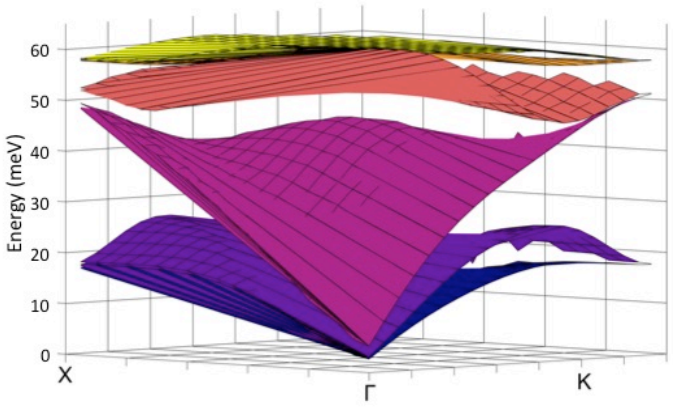

Figure 3. 2D phonon dispersion surfaces for Silicon in the [110] zone.