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Localized signals in vibrational STEM-EELS

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To date, vibrational EELS experiments in the STEM have achieved a spatial resolution of only several tens of nm at best [1], which is a far cry from the sub-nm resolution routinely achieved in imaging and other forms of spectroscopy. This observation is often explained away using a "delocalization argument", which predicts poor spatial resolution on account of the small energy losses.

Here we describe how the vibrational modes of a material can be mapped with a spatial resolution of the order of one nanometer, a 10-fold improvement on previous works. We use an off-axial collection geometry in EELS (Figure 1). We use boron nitride, a polar dielectric which gives rise to both localized and delocalized vibrational scattering, either of which can be selected in our experimental geometry.

Long-wavelength optical modes can give rise to long-ranged electric fields both inside and outside the sample. Hence, such modes can be excited by beam electrons passing at relatively large distances, up to the so-called "delocalization distance" v/ω, where v is the beam electron's velocity and $\hbar\omega$ is the vibrational mode energy. For $\hbar\omega \sim 100$ meV, we obtain $v/\omega \sim 1$ μm, and indeed we can detect the excitation of these modes—the dipole scattering—even when our electron beam is made to pass hundreds of nm outside the sample. Such long-wavelength excitations necessarily involve small momentum transfers and scattering angles, the latter being ~ 1 μrad (Figure 2a, cyan regions).

Shorter wavelength vibrational modes, on the other hand, involve rapidly modulated atomic displacements, for which long-ranged electric fields largely cancel out. Such modes can only be excited by beam electrons passing in the immediate vicinity of an atomic ion—the localized scattering—facilitating higher spatial resolution. The localized scattering involves larger momentum transfers and scattering angles (Figure 2a, magenta regions). Hence to detect the excitation of such modes, we use an off-axis EELS collection aperture.

Figure 2b and 2c compare the spatial resolutions obtained using the dipole signal and the localized signal from a 70-nm thick sample of [001] BN. The electron probe traverses the indicated path across the edge of the BN crystallite. The simultaneously acquired annular dark-field (ADF) signal is also shown for comparison. The dipole signal is seen to extend hundreds of nm outside of the sample, whereas the localized signal is contained to within at least 2 nm of the sample (note the different spatial scales in Figures 2b and 2c). The spatial resolution of the localized signal is the same as the ADF signal, as would be expected given the description above.

Our experimental results are well supported by quantum-mechanical calculations, and should reconcile current controversy regarding the spatial resolution achievable in vibrational EELS in the STEM. With further improvements in energy resolution, combining nanometer-scale vibrational analysis with the other high-spatial- resolution signals available in the STEM should provide an extremely powerful toolkit for nanomaterials analysis [2].

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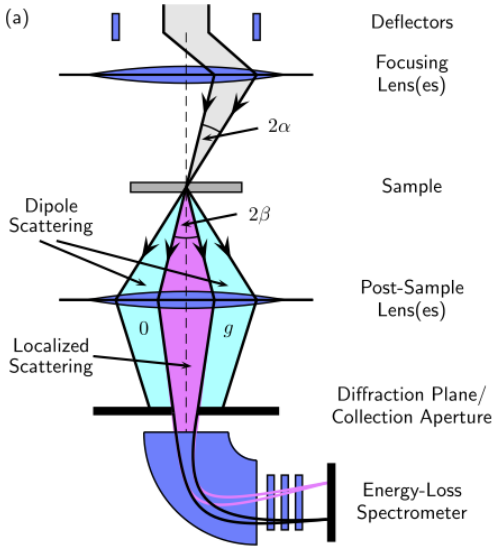

Figure 1. Off-axis optical geometry for localized vibrational scattering.

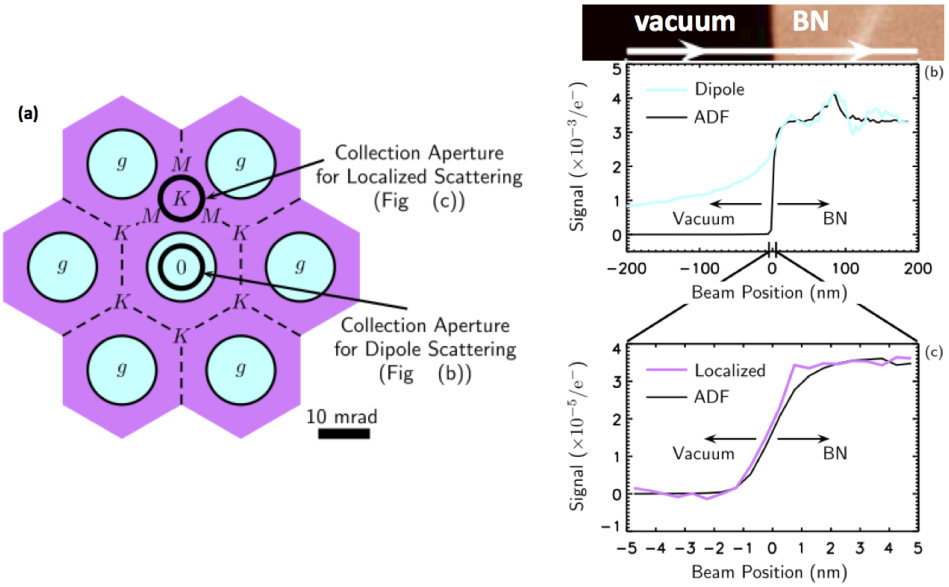

Figure 2. (a) Diffraction pattern of [001] BN showing aperture positions for dipole and localized scattering. Dipole (b) and localized (c) signals obtained as the probe traverses the edge of the BN crystallite. The ADF signals are also shown for comparison. Note the change in spatial scale in (c). The spatial resolution of the localized vibrational signal is 1.9 nm.

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