

Atomically Resolved Vibrational Spectroscopy in the Electron Microscope

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Lattice dynamics in solids, described in terms of quantized collective vibrational excitations or *phonons*, play a major role in such phenomena as superconductivity, electrical conductivity, thermal transport and structural phase transitions. Phonons can be probed using electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM), with a spatial resolution exceeding that of more conventional techniques such as inelastic x-ray and neutron scattering, or optical spectroscopies [1,2]. With an aim to take full advantage of the $\leq 1 \text{ \AA}$ electron probe available in state-of-the-art STEMs, the possibility of atomically resolved vibrational spectroscopy has been discussed in the electron microscopy community. Improving on a previously reported demonstration of $< 2 \text{ nm}$ spatial resolution [3], we show that atomically resolved vibrational spectroscopy is possible in the electron microscope [4].

Using an off-axial collection geometry (see EELS aperture position “B” in figure 1a) allows for producing atomically resolved phonon structure images (figure 1d) by integrating over loss peaks in a vibrational EEL spectrum image of hexagonal boron nitride (hBN), attributed to the excitation of longitudinal (L) and transverse (T), optical (O) or acoustic (A) phonon branches (figure 1b). The lattice contrast in the LA-TA and LO-TO maps in figure 1d is attributed to localised inelastic *impact* scattering, not preservation of elastic contrast, in agreement with our simulations. This is further confirmed by the fact that the contrast of these phonon maps differs significantly from that of the corresponding quasi-elastic zero loss peak (ZLP) map. Effectively displacing the spectrometer aperture away from the optical axis (using e.g. a “diffraction shift” control) reduces the relative spectral contribution of elastic and delocalised inelastic *dipole* scattering with respect to that of impact scattering, making possible the acquisition of phonon structure images of hBN using the Daresbury Nion UltraSTEM100MC, with reasonable signal-to-noise. The advantage of an off-axis collection geometry is clear from comparing the lattice contrast in the off-axis phonon maps (figure 1d) to the fairly poor contrast in the on-axis (“A”, figure 1a) map (figure 1c) of the phonon loss peak (figure 1b), attributed to the excitation bulk optical (LO-TO) modes and associated phonon polaritons (PhPs). Atomically resolved vibrational spectroscopy in the STEM could be particularly useful for probing effects induced by vacancies, dopants and grain boundaries, and other localized modifications of a materials vibrational response, at finite wave vectors. Our approach provides complementary information to that of nanoscale phonon dispersion mapping [5, 6]; possible advantages of applying both methodologies to the same materials system will be discussed [7].

References:

[1] OL Krivanek et al., Nature **514** (2014), p. 209.

[2] MJ Lagos et al., Nature **543** (2017), p. 529.

[3] C Dwyer et al., *Physical Review Letters* **117** (2016), 256101.

[4] FS Hage et al., *Physical Review Letters*. **122** (2019), 016103.

[5] FS Hage et al., *Science Advances* **4** (2018), eaar7495.

[6] RJ Nicholls et al., arXiv:1804.10475.

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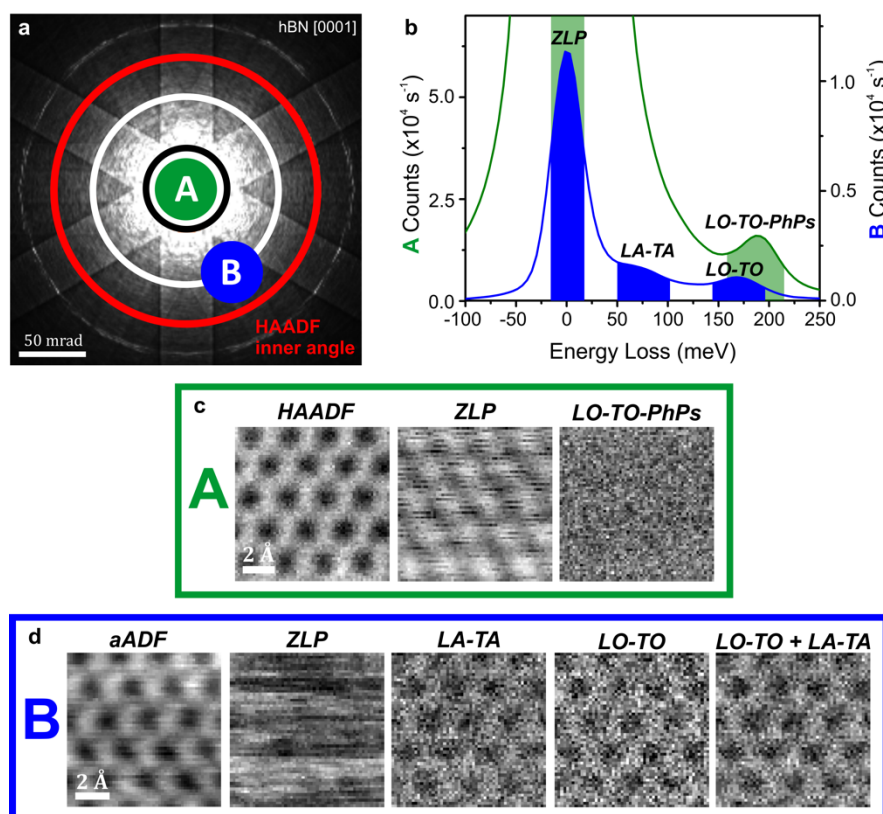


Figure 1. (a) Sketch of the experimental geometry, superimposed on a simulated hBN diffraction pattern. Spectrometer aperture size and effective positions are indicated by solid discs. Circles indicate the circumference of the bright field disc (black), the inner angle of a typical high angle annular dark-field (HAADF) detector (white) and the inner angle of the HAADF detector in the present experiments (red). (b) Spectra for aperture positions A and B, summed over the data sets in (c) and (d). (c) HAADF image and spectrum maps integrated over the energy ranges indicates in (b), for aperture position A. (d) “Asymmetric” annular-dark field (aADF) image and spectrum maps integrated over the energy ranges indicated in (b), for aperture position B. Images were acquired with the HAADF detector centred on either the optical axis (c, position A) or on the EELS aperture in position B (d, thus resulting in “asymmetric integration” in angle space). Data shown in (b)-(d) were acquired from an AA’ stacked 28 ± 6 nm thick hBN flake, with the electron beam incident along [0001].