Phonon Spectroscopy at Atomic Resolution in the STEM

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Phonons are central to modern physics, underpinning our understanding of phenomena such as superconductivity, thermal transport or even structural phase transitions, which in turn govern the properties of every-day functional materials. It is believed that the structure and chemistry of materials, even at the single atom level, can affect the nature, frequency and behaviour of phonons.

Recent methodological developments have shown how electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) can be used to study the dispersion of phonons at the nm-scale, by carefully adjusting optical parameters to balance spatial and momentum resolution. These initial results demonstrated the ability to carry out momentum-resolved vibrational spectroscopy of volumes of material orders of magnitude smaller than previously possible [1,2].

Here we demonstrate for the first time the ability to map, or image, at atomic resolution, the intensity variations of phonon modes in a thin crystal of hexagonal boron nitride using high resolution STEM-EELS. As for momentum-resolved vibrational spectroscopy, the methodology developed in this work consists in displacing the EELS collection aperture away from the optic axis of the instrument. In this case, however, the probe-forming optics are set up to maintain atomic-level spatial resolution and the EELS aperture is displaced to high angles typically used for annular dark field imaging. In this collection geometry, the contribution of electrons that have undergone elastic and non-local dipole scattering is minimised, favouring instead the highly localised impact transitions in the recorded spectrum. The angular (radial and azimuthal) variations of the spectroscopic signal are discussed, as are the differences in observed contrast if attempting similar experiments in an on-axis EELS collection geometry instead.

Simulations based on the quantum excitation of phonons (QEP) formalism show good agreement with the experimental data and reproduce the atomic-resolution contrast obtained in the experimental images. We thus demonstrate conclusively and directly that inelastic scattering associated with phonon excitations plays a central role in generating the contrast widely used for atomic resolution high angle annular dark field imaging [3].

In addition to providing insights into the image formation mechanism in the electron microscope, these results demonstrate a practical methodology to probe vibrational phenomena at the atomic scale, orders of magnitude higher than previously possible. This is a step change in the experimental toolbox available to physicists, chemists or materials scientists and a further exciting application of recently developed high energy resolution monochromators [4].

References:

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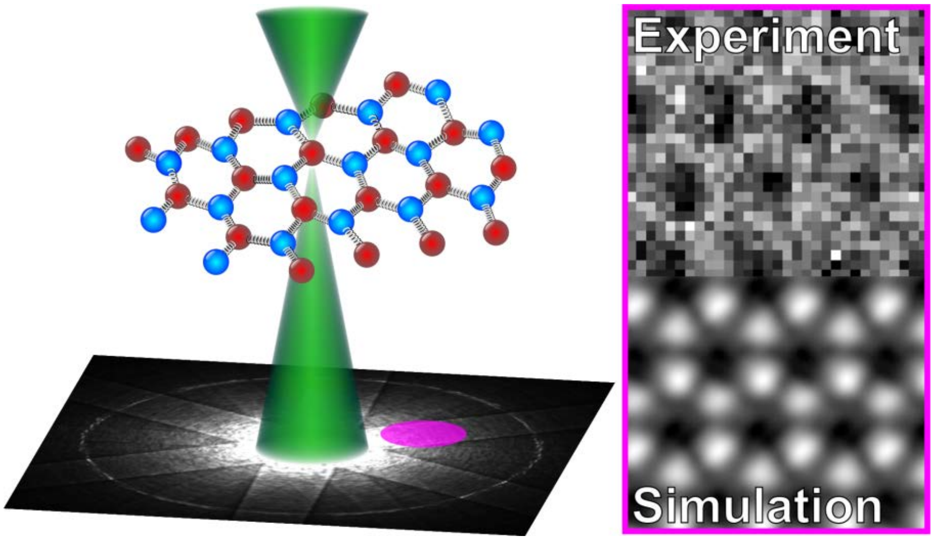

Figure 1. *Left:* Schematic representation of the experimental geometry used for the experiments, carried out on a Nion UltraSTEM 100MC 'Hermes' operating at 60kV. The EELS collection aperture (represented by a purple disc overlaid on a simulated diffraction pattern) is positioned away from the optic axis in the far field to collect electrons scattered from the hexagonal boron nitride sample to high angles. *Right:* An experimental image obtained by integrating over a ~50-200meV window the EELS signal collected in this off-axis geometry is compared to a simulation of the inelastic signal based of the Quantum Excitation of Phonons model.