

## Momentum-resolved phonon spectroscopy in the transmission electron microscope

Hage, F.S.<sup>1</sup>, Nicholls, R.J.<sup>2</sup>, Yates, J.R.<sup>2</sup>, McCulloch, D.<sup>3</sup>, Lovejoy, T.C.<sup>4</sup>, Dellby, N.<sup>4</sup>, Krivanek, O.L.<sup>4</sup>, Bugnet, M.<sup>5</sup>, Radtke, G.<sup>6</sup>, Allen, L.J.<sup>7</sup>, Refson, K.<sup>8,9</sup> and Ramasse, Q.M.<sup>1,10</sup>

<sup>1</sup> SuperSTEM Laboratory, United Kingdom, <sup>2</sup> University of Oxford, United Kingdom, <sup>3</sup> RMIT University, Australia, <sup>4</sup> Nion Company, United States, <sup>5</sup> University of Lyon, France, <sup>6</sup> Sorbonne Universités-UPMC Université Paris 06, France, <sup>7</sup> University of Melbourne, Australia, <sup>8</sup> STFC Rutherford Appleton Laboratory, United Kingdom, <sup>9</sup> Royal Holloway, United Kingdom, <sup>10</sup> University of Leeds, United Kingdom

Advances in electron source monochromation are now allowing vibrational modes to be probed at high spatial resolution by electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) [1, 2]. The EEL mode momentum transfer dependence (*i.e.* dispersion) can provide information about a material system that is often obscured in spectra acquired using experimental geometries optimized for high spatial resolution. However, momentum-resolved vibrational measurements have so far been limited to "bulk" techniques (*e.g.* inelastic x-ray and triple-axis neutron scattering spectroscopies), the average surface response (*e.g.* reflection EELS) or small momentum transfers (*e.g.* optical techniques).

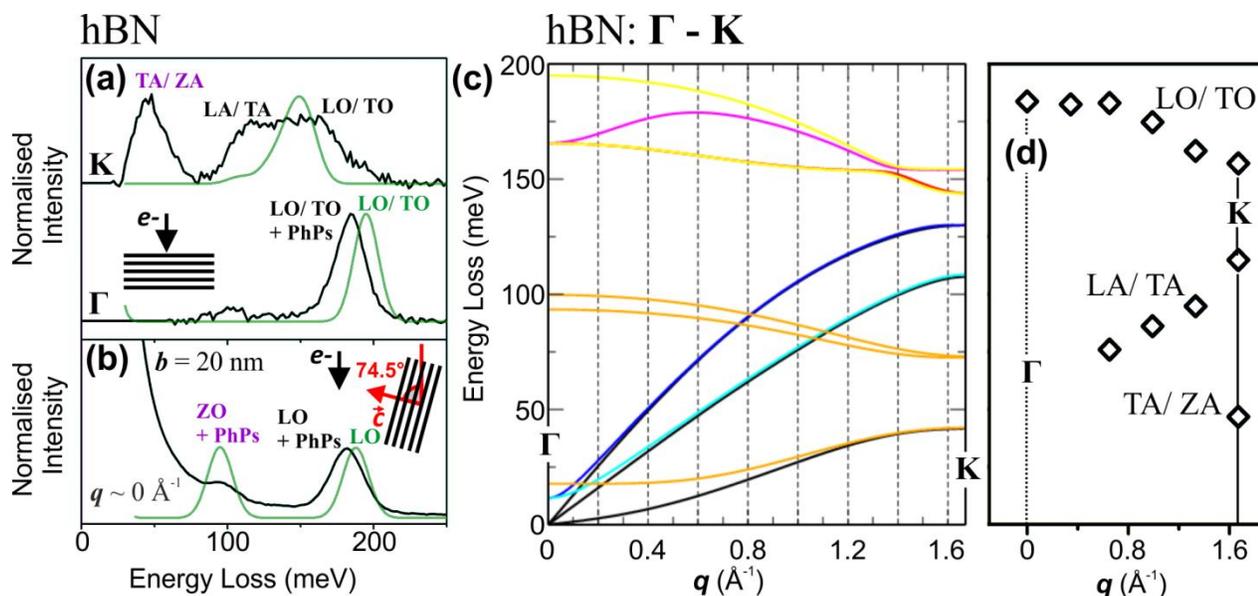
Here, we present a highly flexible combined experimental and theoretical methodology for acquiring and interpreting phonon dispersions across the first Brillouin zone (BZ) in the electron microscope. Carefully balancing the intrinsic trade-off between simultaneously achievable resolutions in real and momentum space, we map the vibrational response of two polymorphs of boron nitride (BN) along different directions of their respective BZs, using a  $\sim 1$  nm electron probe. Effectively, we acquire spectra akin to those of inelastic x-ray and neutron spectroscopies while probing a sample volume that is  $\sim 10^{10}$ - $10^{20}$  times smaller [3].

The experimental data show remarkable agreement with *ab initio* calculations; acoustic (A), optical (O) and anisotropic phonon mode contributions are clearly identifiable in the experimental spectra. Fig. 1a shows experimental and modelled EEL spectra at the  $\Gamma$  and  $K$  points of the first BZ of hexagonal (h) BN, while Fig. 1b shows an "aloof" spectrum. Modelled and experimental hBN phonon dispersions are shown in Fig. 1c and d, respectively. For small momentum transfers, spectra are dominated by a peak comprising contributions from the longitudinal (L) and transverse (T) optical phonon branches as well as so-called "phonon polaritons" (PhPs) [2]. At larger momentum transfers in-plane LA, TA, LO and TO phonon branches all contribute. At the  $K$  point, the contribution of the out-of-plane TA and ZA branches is attributed to a combination of experimental geometry and Ewald sphere curvature. Fig. 1b also demonstrates that certain experimental geometries allow for a significant contribution of the out-of-plane ZO branch (and associated PhPs), emphasising the importance of carefully characterising the beam geometry for vibrational spectroscopy in the STEM [3].

A similar approach is used to probe the vibrational mode momentum dependence in boron suboxide (B<sub>6</sub>O), a superhard material, illustrating the versatility and broad applicability of this methodology. EEL spectra acquired in "aloof" geometry are interpreted on the basis of *ab initio* calculations [4], leading to the identification of vibrational modes responsible for the observed spectral features. In combination with more conventional STEM-EELS techniques, the present methodology is particularly well suited for the analysis of materials systems where nano-to-atomic scale structure and chemistry significantly affect the vibrational response [3].

## References

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**Fig. 1** (a) Selected experimental (black) and modelled (green) momentum resolved hBN EEL spectra. (b) "Aloof" hBN EEL spectrum, acquired at a beam incidence of  $74.5^\circ$  to the crystallographic c-axis and at an impact parameter of  $b = 20$  nm. In-plane (black) and out-of-plane (purple) phonon mode contributions are indicated. (c) Modelled and (d) experimental phonon dispersions, where  $q$  is the wave vector.

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