Momentum resolved spectroscopy of the dielectric response by TEM

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Considering dielectric properties of 2D materials, specific questions arise among the screening effects of charge carriers or effects induced by the substrate and highlight the necessity of studying these properties on free standing pristine layers. This can be done using electron energy loss spectroscopy in the low loss energy range (Low-EELS) related to interband and plasmons excitations [1]. Furthermore, in contrast to standard optical spectroscopies, the transfer momentum dependence of the excitations is accessible from the measured loss function provided to operate an angular resolved EELS [1]. Measuring the q dependence of the loss function needs to build a data cube in the diffraction space relying energy losses and q vectors in the diffraction plane [2, 3]. In this work, this is operated employing an electron energy spectroscopic set up in a Libra 200 TEM equipped with an electrostatic monochromator operated in the 40-80 kV range, an in-column corrected omega filter and a CCD camera thanks to which a spectral resolution below 100 meV can be achieved at 40 kV [4]. This set-up provides high quality energy-loss spectra in the form of ω-q maps obtained by selecting a q direction thanks to a slit implemented at the entrance of the omega filter and allows also for the imaging of energy-filtered diffraction patterns. These two acquisition modes provide complementary pieces of information, offering a global view of excitations in reciprocal space. We present here the capabilities of this setup through the study of various 2D layered materials. The Figure 1 displays low losses spectra of pristine mechanically exfoliated phosphorene flakes showing a clear energy upshift of the excitation onset upon thickness decreasing. Optical gaps deduced from these spectra indicate values varying from 1 eV to 1.9 eV between the 3L and the monolayer, which are very close to theoretical predictions [5]. In the same way a blue shift from 1.4 to 1.8 eV of the optical gap has been measured in MoS_2 between multilayers and the monolayer.

Figures 2 and 3 summarize measures of the low losses associated with interband and /or plasmon excitations performed on hexagonal boron nitride single crystals cut along different directions of the Brillouin zone [4]. First, energy filtered patterns in the basal plane reveal the symmetries of the dipole matrix elements involved in the observed transitions and reveal the direct and indirect nature of the excitations observed for the low losses at 8 and 12 eV respectively. Moreover, by comparing these patterns with our specific ab initio calculations, we show that we are able to relate the range of applicability of ab initio calculations to the anisotropy of the sample and assess the level of approximation required for a proper simulation. Second, intensity profiles extracted from ω-q maps recorded along different directions of the Brillouin zone allow to illustrate that our method provides results which quality is comparable to that obtained from non resonant x-ray inelastic scattering [6] but with advantageous specificities such as an enhanced sensitivity at low q and a much greater simplicity and versatility that make it well adapted to the study of two-dimensional materials and related heterostructures.

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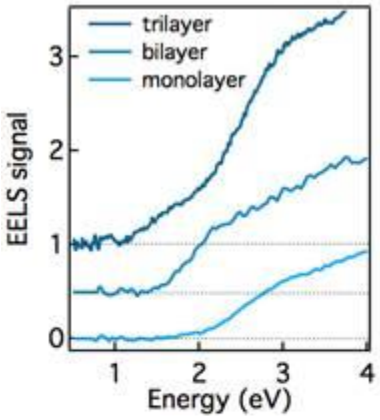

Figure 1 : Evolution of black phosphorus bandgap versus thickness

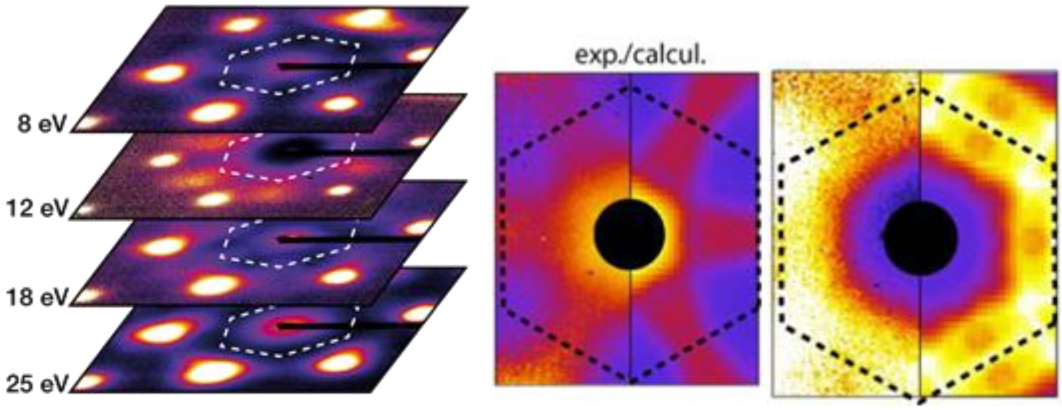

Figure 2 : (left) Energy filtered scattering patterns of hBN in the basal plane measured. Comparison between measured and calculated loss function at 8 eV (middle) and 12 eV (right). Dashed lines represent the Brillouin zone boundary.

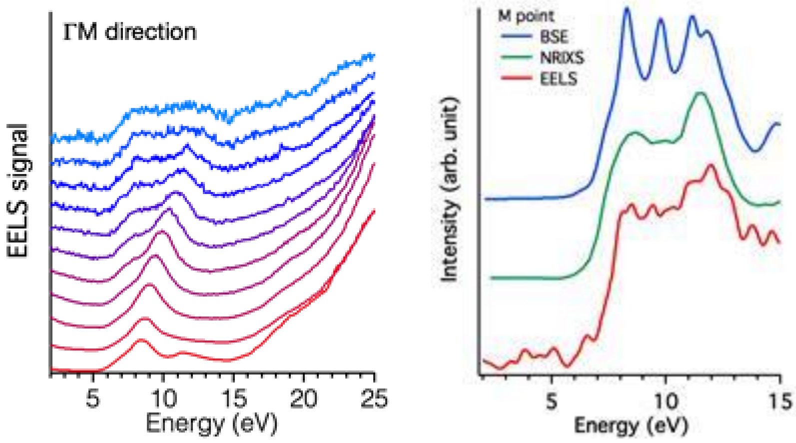

Figure 3: (left) dispersion of the loss signal through the Brillouin zone from Γ (red) to the M point (light blue). (right) Benchmark between EEL measures, NRIX measures from [5] and Bethe-Salpeter calculations at the M point of the Brillouin zone of hBN.