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High spectral resolution EELS to probe optics at the nanometer scale

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The remarkable energy resolution and control achievable in all-optical experiments makes it a hard contender against new designs and developments in other spectroscopies, at least in the optical range. However, this high precision means that even nanometer scale changes to the object under study have a detectable spectral effect . For example, a 10 nm length change on a micrometer-long metallic rod leads to an energy shift of the order of 1 meV, roughly. Hence, the necessity of coupling high spatial resolution to high spectral resolution. Up until recently, this bridge was crossed by performing complementary electron microscopy measurements at high spatial resolution in addition to optical measurements either ex or in situ.

Yet, the use of electron energy loss spectroscopy (EELS) in different configurations and with increased spatial and spectral resolutions has shown there are many benefits in using electron beams for spectroscopy, at least where nanometer scale features are relevant. More importantly, the remarkable spectral resolution in experiments with focused electron beams [1-4] achieved in the previous few years makes EELS a powerful companion to all-optical spectroscopies. Finally, EELS in a transmission electron microscope has the added benefit of direct access to the reciprocal space. In this contribution, we will describe two groups of experiments to demonstrates our current possibilities in the reciprocal and real spaces.

First of all, the band structure of Al plasmonic crystals with > 100 nm lattice parameter and >10 µm lateral size were studied, aiming at identifying an energy gap in their plasmonic band structure. Because of the large lattice parameter an angular resolution better than 1 µrad is necessary. This, has been possible for decades using cold field emitters for electron diffraction. However, for plasmonic crystals, most of the interesting applications are in the visible or IR range. Hence, EELS experiments were limited due to large tail of the zero-loss peak. Moreover, the necessity of measurements across the whole Brilloin zone imposes large exposure times, due to weak signals. Therefore, experiments were limited by the time-stability of the zero-loss peak position and of the microscope overall alignment.

In our experiments, we were able, by using an electron beam with sub-µrad convergence and sub-100 meV energy resolution associated with high temporal stability, to show the opening of a band gap in the plasmonic band structure of an Al crystal with a triangular lattice. This gap is opened between 1.27 eV and 1.92 eV. More interestingly, we have shown that a defect in this lattice introduces an energy level within the band gap, in close analogy to what happens in a "normal" atomic crystal.

Concerning high spectral resolution (< 10 meV) at high spatial resolution (< 10 nm), we will discuss the mapping of surface phonon modes on h-BN flakes of varying thickness (Figure 2). As it has been discussed in the literature, EELS measures the Fuchs-Kliewer (FK) modes [5,6]. The physics of these excitations is very similar to that of surface plasmon modes in metal nanoparticles [6]. As expected we observe two FK modes at 173 meV and 195 meV. The intensity of these modes changes as a function of the thickness of the h-BN flake. Initially with the electron beam in aloof geometry only the lower energy mode is observed. The intensity of the second mode increases as a function of the thickness of the flake. This is expected because of the symmetry of the eigencharge of this mode, which is symmetric between the two surfaces (similarly to what is observed in a thin metal film).

Finally, the experiments presented above were performed on the ChromaTEM microscope, a modified Nion Hermes 200 with a cold sample stage. If time allows, we will present some more recent results on nanoscale plasmon physics obtained with this machine.

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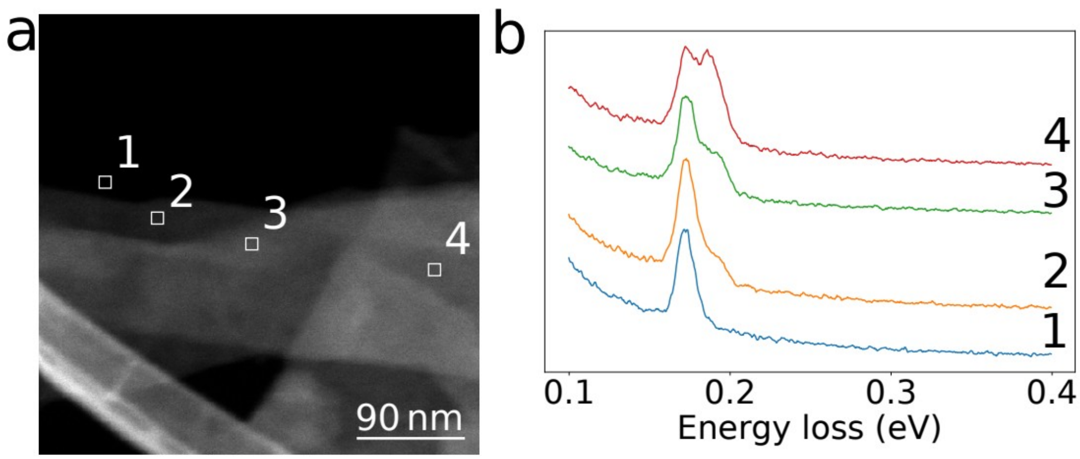

Figure 1: a) High angle annular dark field image of an h-BN flake. **b)** Four spectra averaged from an hyperspectral image in the regions marked 1-4. Initially, with the beam in vacuum, only a single peak is observed at 173 meV. As the beam is positioned towards thicker parts of the flake, a peak at 195 meV appears, with increasing intensity.

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