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A spectromicroscope for nanophysics

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ABSTRACT

The new generation of spectromicroscopes opens up new fields of nanophysics. Beyond the impressive spatial and spectral resolutions delivered by these new instruments - an obvious example being the Hermes machine conceived, designed and built by O. L. Krivanek, who is honoured in this journal issue - here we wish to address the motivations and conditions required to get the best out of them. We first coarsely sketch the panorama of physical excitations worth motivating the use of ultra-high resolution spectroscopy techniques in STEMs. We then give general considerations on the use of combined spectroscopy techniques, reciprocal space measurements and additional time-resolved experiments to complement the wealth of the physical insights provided by the new-generation spectromicroscopes. We then comment on the newly enhanced mechanical and high voltage stabilities and their effects on the accuracy of spectroscopic measurements. The use of temperature-dependent experiments, to bring electron spectroscopy techniques to the standard of other condensed matter physics techniques such as optical and X-ray spectroscopy, is also described. We finish by evaluating the impact of other breakthrough developments, such as energy gain electron spectroscopy or electron-phase manipulation, on the use of ultra-high resolution spectromicroscopes.

1. Introduction

In 2010, the French government launched an ambitious research funding programme called “Equipements d’Excellence” (EQUIPEX, Excellence Instruments), to fund instrumentation like modern transmission electron microscopes (TEM) or nuclear magnetic resonance (NMR) apparatus that were missing in the French research landscape. The project lead by one of us (OS), and grouping many laboratories in the Orsay vicinity, consisted in three parts. The first concerned a versatile microscope (NANOTEM), the second an *in-situ* microscope (NANOMAX), and the last one a microscope dedicated to high spectral and spatial resolution spectromicroscopy (CHROMATEM).

CHROMATEM was foreseen to combine high spatial and spectral resolution in electron energy loss spectroscopy (EELS) yet with high currents reaching the detectors, a light injection/detection system and a low- temperature stage, among other specifications. It aims at tackling new physical problems that share the need to access the electronic and/or optical properties at the nanometer scale or at single atomic column positions with spectral resolutions which were not available at the time of writing the proposal. Very generally, such a microscope is supposed to make possible the exploration of several open issues in nanophysics, including metal-insulator transitions in systems with strong electronic correlations, photomagnetic mechanisms in molecular magnets, optoelectronic properties of semiconductor nanostructures and metamaterials and interface physics in oxitronics and ferroelectric devices (see Fig. 1). Back in 2010, we were betting on the idea that the pioneering monochromated works [1,2], the increasing success offered by 21st century monochromators [3–5], signalled the likehood of breaking the sub-50 meV/high spatial resolution limit. The recent breakthroughs in the field [6–8] exceeded our wildest expectations.

This project for a spectromicroscope for nanophysics got funded in early 2011, and we finally ordered an improved version of the monochromated NION HERMES [7,9] after a 1 year tender in 2012. Therefore, when the two editors of this issue dedicated to O. L. Krivanek asked us to write, “[...] as EELS experts, long-time followers of Ondrej’s work and user of his instruments, [...] a personal perspective on the application and development of STEM / EELS / CL [...]”, we were excited at presenting the extraordinary specifications of this “spectromicroscope” dedicated to nanophysics, together with the first experimental results obtained on CHROMATEM. We felt this would be the perfect way of honouring a scientist who has devoted his life to building disruptive electron microscopes and electron spectrometric systems.

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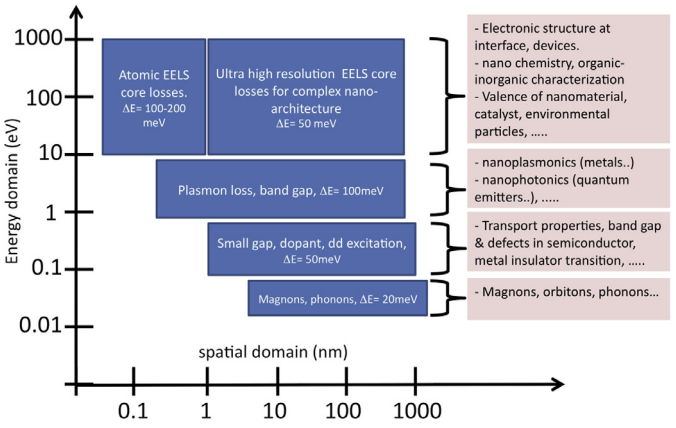

Fig. 1. Energy and spatial domains foreseen to be covered by the CHROMATEM EELS/CL spectro-microscope at the time of the writing of the project. A few examples of the fields of application are also noted. Related linewidths are indicated as ΔE.

In this tribute paper, we thus present various ideas that guided us when defining the specifications of the CHROMATEM project, illustrated with experiments or principles which inspired us at the time of writing the proposal or which have been performed since the arrival of the new generation of scanning TEM (STEM) dedicated to spectromicroscopy. We also describe how these specifications have been updated in view of some amazing new developments in the field, and tried to illuminate our discussions with milestone works from O. L. Krivanek. Unfortunately, CHROMATEM is still not delivered at the time of writing, and therefore we cannot confront some of our guesses with real examples taken with this instrument. Nevertheless, we hope that the present paper, reviewing conceptual and technical challenges, will be both a relevant tribute to O. L. Krivanek, and of some use for other scientists that are tackling the exciting new fields opened by the new generation of spectromicroscopes.

In the first section, we quickly discuss the physical excitations of interest explaining the need for high resolution STEMs. In the following sections, we give some physical reasons why experiments going beyond the sole use of high resolution EELS are needed. This will encompass the use of combined spectroscopy techniques (here a little-known and amazing early work of O. L. Krivanek will be disclosed) and the motivations for working in reciprocal space. Finally, the interest of doing time-resolved experiments in addition to experiments in the spectral domain will be emphasised. With the constantly improving spectral resolution of lastest generations microscopes [3,6,7,10,11], one may ask two questions that Section 6 will try to answer. What is the need for energy resolution higher than typical linewidths - in the case of core-losses or plasmons, for example? More generally, why are high stability and better detectors needed to really benefit from these improved spectral resolutions? This section will borrow ideas from two important papers by O. L. Krivanek. The first [12] deals with the detection efficiency of EELS detectors, the second [13] with the necessary requirements for building modern spectromicroscopes beyond the sole increase in spatial resolution. The increase in spectral resolution in EELS (but also in cathodoluminescence, CL, or X-ray luminescence techniques) now makes it possible to detect minute modifications in spectra, possibly unveiling interesting physics. Such possibilities put modern microscopes in the position to tackle fields conventionally studied with other tools of materials science, solid state physics or optics. Therefore, in Section 7 we will underline the need to equip any spectromicroscope with the capability of monitoring the temperature over large ranges, as is usually mandatory in any serious use of more conventional characterisation tools. Finally, new trends in using exotic types of electron beams (pulsed, phase-shaped...) with be discussed in Section 8.

2. Physical justification of the need for increased spectral resolution and range

Fig. 1 presents several physical excitations and phenomena of interest in nanophysics that could be probed specifically through the use of either a highly monochromated (S)TEM or a (S)TEM equipped with a CL system. The excitations are plotted as a function of their typical energy and space scales, and their typical linewidths are given. We note that the current performances of the actual monochromated spectromicroscopes fitted with EELS [6,7] and CL systems [14,15] should indeed allow the exploration of the given excitations.

Following the general nomenclature of EELS, two energy regions are emphasised:

(a) In the energy domain from around 50–1000 eV, involving core-loss excitations, increased EELS resolution offers new possibilities (such as more accurate valency, charge transfer, spin state measurements...) for the atomic resolution studies of the excitation spectra of various materials, such as functional oxides with long lifetime electronic excitations. This obviously concerns correlated electron systems, with d- (transition metal) or f- (rare earth) narrow bands. The EELS spectra may also exhibit subtle changes (metal-insulator transitions, spin transitions, ferroelectricity signatures ...), which are only visible at high energy resolution. Targeting such physical phenomena is of course inspired by the success of synchrotron radiation-based spectroscopies (X-ray absorption spectroscopy -XAS-, X-ray magnetic circular dichroism -XMCD- ...). With modern spectromicroscopes, we can in addition benefit from spatial resolutions well below 20 nm which XAS and XMCD cannot easily overcome.

(b) In the low-loss energy domain from typically a few tenths of an eV to a few eV, the improvement in EELS energy resolution down to around 10 meV is necessary in order to reduce the intensity of the zero-loss tail and to probe the electronic response from the visible range down into the infrared. This enables the measurement of plasmons, band gaps, excitons (for example, p-d excitations in the case of transition metal oxides), d-d excitations and possibly magnons in correlated electron systems, and phonons, with a nanometer-scale resolution.

Some physical excitations of interest have been just quickly adressed here (others will be given later). Now that the scientific community is able to tackle their study in a STEM, many additional physical and technical points that are worth addressing at this stage will be given in the next sections. However, before entering these details, it is important to answer a recurrent question addressed to electron (spectro)microscopists: how can we justify the use of expensive spectroscopic tools when other probes reach orders of magnitude better spectral resolution with, in some cases, even better spatial resolution? For example, STED (stimulated emission depletion) can localise in 3D a single point defect with sub-nanometric precision [16] although it is a far-field technique; scanning tunnelling microscopy luminescence has mapped optical signals with near-angström resolution [17], and more recently Raman (phonon) signals with similar spatial resolution [18]. There are several answers to this question. The first is that STEM techniques are usually much more universally applicable, as most of the above-mentioned techniques rely on specific effects (plasmon enhancement, stimulated depletion ...) that only exist for rather small categories of objects. A second answer relies on the observation that atomic resolution might be necessary in order to understand the physics of a given object, in combination to (optionally) non-atomically resolved electron spectroscopy. For

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