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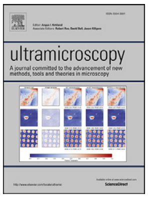

A spectromicroscope for nanophysics

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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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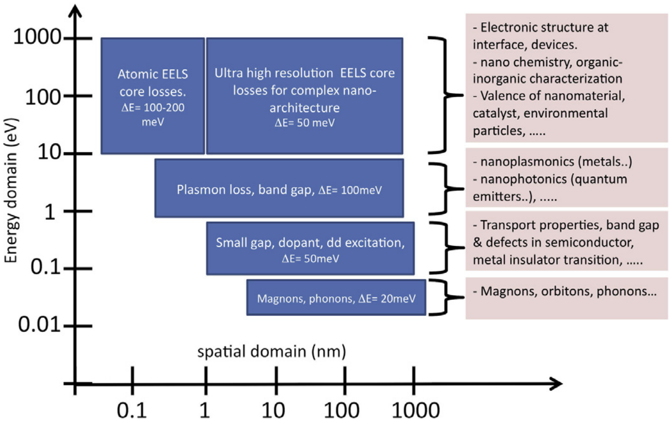

Fig. 1. Energy and spatial domains foreseen to be covered by the CHROMATEM EELS/CL spectro-microscope at the time of the writing of the project. A few examples of the fields of application are also noted. Related linewidths are indicated as ΔE.

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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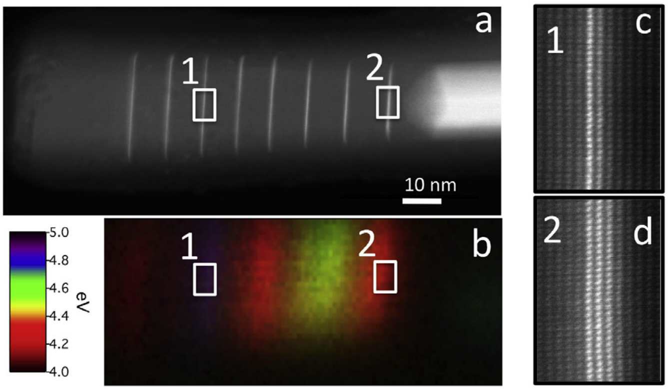

Fig. 2. CL spectrum-image of quantum emitters. a. HAADF image of GaN quantum discs (white contrast) contained within an AlN (grey) nanowire. b. Corresponding CL spectrum-image image of the structure (scale is the same as the HAADF image). This image is generated by colouring each filtered map of the dataset according to its energy, weighting each pixel of each map by its intensity and summing all the resulting images. The false colour scale is indicated. This simplified representation of the spectrum-image illustrates clearly that each quantum disc emission can be straightforwardly recovered. c and d: high resolution images of the quantum discs framed in a and b. The correlation between CL spectrum-image and HAADF shows that, as expected, the thinner a quantum disc, the higher its luminescence energy. Additional elemental mapping is also possible; see e.g. [20]. Data courtesy of S. Meuret and L. H. Galvão Tizei.

example, the optical signal acquired through cathodoluminescence from a series of GaN quantum wells in Fig. 2, means little if it is not compared with the atomic structure of each well imaged in parallel. Comparing both, one can for example see in Fig. 2 that the thinner the well, the higher the emission energy value [15]. More generally, the multidetection capabilities in STEM considerably widen the interest of the technique.

3. The need for combined spectroscopic measurements

In the preceding section, the different physical excitations were categorised using typical quantities such as “energy” and “linewidth”. Such quantities are implicitly assumed to be the same whatever the technique used to probe them. This is however not true. Such quantities might be perfectly defined for an excitation. However, different spectroscopic techniques provoke this excitation in different ways, leading to related but different information. Indeed, the main spectroscopy techniques of electron microscopy can be split in two categories, namely EELS on the one hand, and the luminescence techniques: energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS) or soft X-ray dispersive spectroscopy (SXES) and CL, on the other. EDS/WDS/SXES and CL are luminescence and/or scattering spectroscopies, while EELS is an absorption (more rigorously an extinction) spectroscopy. Therefore, although core-loss (resp. low-loss) EELS spectra share some resemblance with EDS/WDS/SXES (resp. CL), they are fundamentally different in nature.

The difference between EELS and EDS/WDS/SXES has been comprehensively reviewed in [19]. To summarise, EELS spectra, in the core-loss region, correspond to transitions from the inner-shell states to the conduction band. The hole left in the inner-shell may then be filled by available electrons in the valence band or other inner shell states, resulting with a certain probability in an X-photon emission. Therefore, the two spectroscopy techniques are quite different: while EELS probes unoccupied states, EDS/WDS/SXES probe occupied states, and the information gained for example from a band of given symmetry might be quite different. This is illustrated in Fig. 3 (top) in the case of the B-K edge in hexagonal boron-nitride. Although displaying a rough resemblance, the two spectra are different. This is to first order related to the differences between the valence band (VB) and the conduction band (CB) density of states (DOS).

Beyond that, it is also striking to note that the electron involved in the formation of a given edge in EELS generally does not trigger emission of the X-ray photon corresponding to the same peak in the EDS/WDS/SXES spectrum [21], and *vice-versa*. Therefore, in addition to the fact that to first order EELS and EDS/WDS/SXES probe different DOS, the difference in the signal generation mechanisms may lead to further differences in the spectra, such as the possibility of core-hole effects in EELS, which are absent in EDS/WDS/SXES [19].

Similarly, differences are also worth noting between EELS and CL, although for other physical reasons; indeed, the CL generation mechanisms are quite different from those in EDS/WDS/SXES. In the visible domain, one needs to consider two types of excitations, namely incoherent and coherent ones. This is discussed in great detail in [15], but here for simplification, we will focus our discussion on two representative cases. These are electron-hole pairs (or excitons) in semiconductors (incoherent excitations), and surface plasmons in metals (coherent excitations).

In the case of semiconductors, the visible-range part of EELS will consist in an absorption band, potentially preceded by an excitonic line (see Section 7) corresponding to transitions from the valence to the conduction band. Additionally, at much higher energy, these transitions add coherently to form a volume plasmon which largely dominates the EELS low-loss region. The CL spectrum origin is more complex in semiconductors [20,23]. In essence, the volume plasmon that has been created during the EELS process, quite far in energy from the visible range, de-excites quickly in the form of hot electron-hole pairs, that thermalise by populating the lowest available energy states. Then, these states may recombine radiatively. Quite generally, in the CL spectrum of semi-conductors, one thus only sees peaks related to transitions between states with the same wavevectors lying at flat parts of the VB and CB. For example, in the case of quantum dots, EELS spectra are composed of a sharp excitonic line followed by a broad absorption band [24], while the CL spectrum consists of a single sharp excitonic line [25]. In addition, the excitonic lines measured in EELS and CL are expected to be shifted in energy with respect to each other because the initial and final excited states are rather different.

In the case of surface plasmons, the CL signal stems from Rayleigh scattering of the electromagnetic field generated by the incoming electron. EELS, in this case, is very close to extinction (scattering+absorption) [26]. Therefore, once again, but for totally different reasons, EELS and CL differ widely. This is illustrated in Fig. 3 (bottom) in the case of a silver nanoparticle [22]. In this example, EELS and CL have been performed on the same silver triangular prism. Both techniques measure the same spatial distribution [22,26] corresponding to the two first plasmon modes, the so-called dipolar ($m = 1$) and hexapolar ($m = 2$) modes. But strikingly, the corresponding energy peaks are shifted with respect to each other. This surprising effect was actually predicted for regular optical spectroscopy techniques in [27]. However, the difficulty of performing the corresponding experiment on a single nanoparticle with conventional optical techniques prevented the observation of this effect prior the first demonstration by combined STEM-EELS and CL [26].

For a long time, the above-mentioned considerations were quite unimportant. Indeed, in almost all labs in the world, the spectral resolution of the different spectrometers, or the available intensity at a given resolution, were not sufficient to reveal these effects at high spatial resolution. With the availability of the new generation of monochromators and/or advances in deconvolution [6–8,28] on the one hand, and the existence of high-efficiency/high resolution STEM-CL [29,30] or WDS [19] on the other, the physics hidden in

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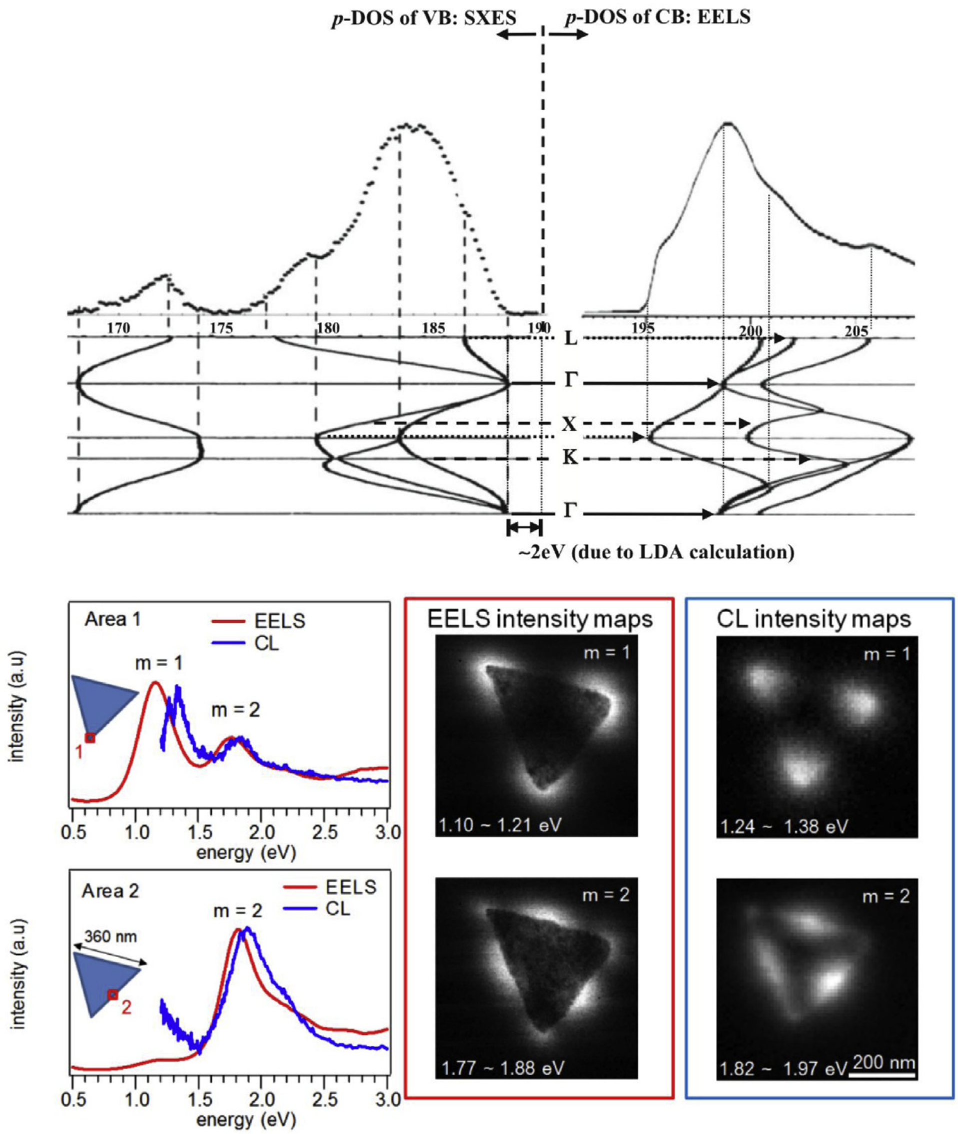

Fig. 3. Difference between absorption and emission spectroscopy. top: In the case of boron K edges in hexagonal boron nitride, comparison between EELS and SXES. EELS gives access to the p-DOS of the conduction band (CB); SXES to the p-DOS of the valence band (VB). Courtesy of M. Terauchi [19], reprinted with permission. bottom: In the case of silver nanotriangles, comparison between EELS and CL. EELS gives access to extinction phenomena, CL to scattering ones. The difference is stronger in the spectra (left) than in the spatial distribution for the dipolar and hexapolar modes. Adapted from [22].

the differences between these techniques can now be systematically investigated.

Beyond the comparison between different spectroscopy techniques, *coincidence* detection might be also desirable. In the context of the CHROMATEM project for example, we wanted to time-correlate EELS and CL. The physical reason for planning coincidence EELS/CL experiments is simple: to answer the question “in a CL experiment, where do the emitted photons come from?” With this aim, the idea is to correlate a given EELS event - the measurement of an energy loss at a given energy - to a given CL event - the measurement of a photon emission at an energy that may be different from that of the EELS event. By measuring the coincidence between these two events, much about the de-excitation physics could be understood.

During the welcome party at the FEMMS 2011 conference, one of us (MK) exposed this exciting possibility to O. L. Krivanek. Quite amazingly, O. L. Krivanek replied that the experiment had already been done by him (and C. Ahn) twenty-six years before... This work was unfortunately not published in a regular journal but in a proceeding [31], see a facsimile in Fig. 4. In this work, time-correlation between broadly energy-filtered EELS and CL signals stemming from a scintillator could be detected, showing differences depending on the EELS energy range. This exciting proof-of-principle experiment, although performed without spatial resolution at that time, demonstrated the feasibility of the measurement, but more importantly, that critical information could be extracted from EELS/CL coincidence experiments. Given the immense progress in spectroscopy since then, there is no doubt that spatially resolved coincidence experiments are now possible.

4. Reciprocal space measurements

In the early days of monochromation in a TEM, pioneering works by the team of Silcox showed amazing spectral resolution (of the order of 100 meV) more than 40 years ago [1,32]. This resolution was much better than the typical linewidth measured on the plasmons of interest in these studies. In these works, the measurements were performed in reciprocal space, leading to the measure-

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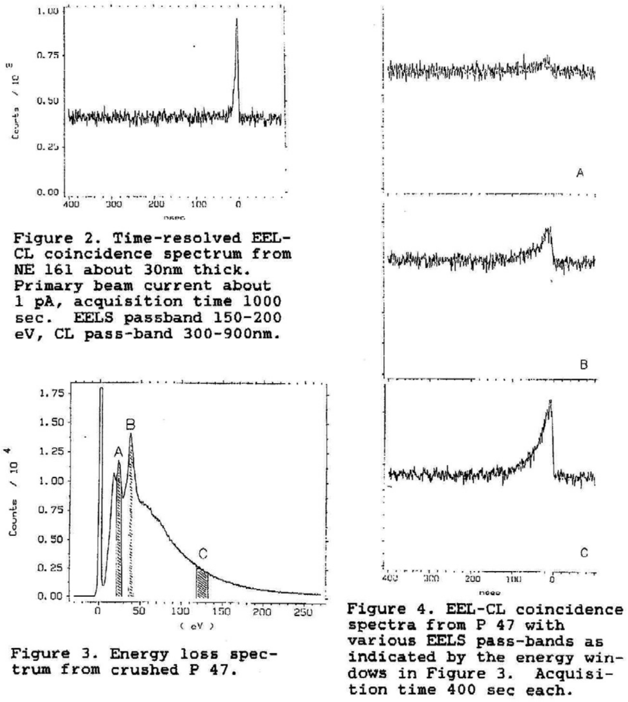

Figure 2. Time-resolved EEL-CL coincidence spectrum from NE 161 about 30nm thick. Primary beam current about 1 pA, acquisition time 1000 sec. EELS passband 150-200 eV, CL pass-band 300-900nm.

Figure 3. Energy loss spectrum from crushed P 47.

Figure 4. EEL-CL coincidence spectra from P 47 with various EELS pass-bands as indicated by the energy windows in Figure 3. Acquisition time 400 sec each.

Fig. 4. Facsimile of the contribution by Krivanek and Ahn [31] showing the first EELS/CL coincidence experiments on a *P*47 scintillator.

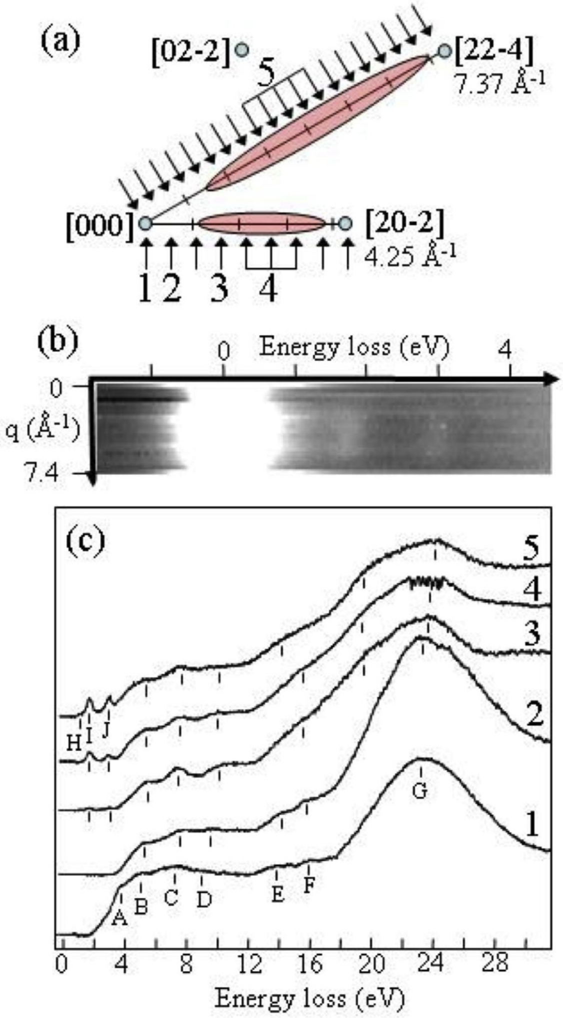

Fig. 5. Angle-resolved NiO EELS. (a) schematic representation of the NiO [111] zone axis diffraction pattern. Arrows indicate positions of collected spectra. The ticks along each direction are spaced by 1 Å^{-1}. The shaded areas identify where d-d transitions mostly show up in the EELS spectra. (b) Dispersion relation along the [22-4] direction. Twenty spectra acquired with a 0.39 Å^{-1} step are represented. The d–d contributions at 1.7 and 3.0 eV and the p-d bandgap at 4 eV can be seen. (c) Representative spectra extracted from the corresponding positions in (a). (H,I,J) clearly identify the d-d transitions within the p-d band gap. From [35].

ment of dispersion relations (i.e energy versus momentum). More recently, the works of the Stuttgart [33] and Ulm [34] teams made it clear that reciprocal space measurements greatly benefit from high energy monochromation, and *vice-versa*.

Indeed, excitations happening in translationally-invariant systems (infinite volume, interfaces, linear object) are better described by momenta along the translation axis (or axes). As soon as one tries to make measurements in real space, the modes of different momenta add up. If they have different energies (i.e they display a non-flat dispersion relation), this leads to a blurred line-shape. This applies to a large variety of bulk excitations, especially acoustic modes which are highly dispersive (for example acoustic phonons), or interface excitations such as surface/interface plasmons, or unidimensional excitations like plasmons in 1D materials (nanotubes)... Therefore, such experiments would be especially interesting for studying low-dimensionality effects.

Getting $\approx$ 10 meV monochromatisation also provides access to new spectral signatures of primary interest in condensed matter physics. For instance, in the case of transition-metal oxides, various degrees of freedom (spin, charge...) are present and playing a role. EELS must be able to probe most of the low-energy excitations related to the presence and interplay of all these degrees of freedom. These are for example the rather localised d-d excitations, charge transfer excitations or excitations related to the long-range order of the system (plasmons, magnons, orbitons, phonons). All the related spectral signatures have different and often complicated real space distributions, or conversely different q-dependence behaviours. In the case of d-d transitions, their high localisation results, in the most simplified case, in almost no q-dispersion. This absence of dispersion is demonstrated in Fig. 5 in the case of NiO [35]. It is also clear from Fig. 5 that the d-d transitions can be observed through q-filtering of the spectra; combined with the absence of dispersion, this makes it possible in principle to map these excitations with high spatial resolution [35]. In a more general case, real and reciprocal space studies of these excitations might be done in a complementary way, notably for transition metal oxide nanostructures such as thin films or super lattices [36], in order to have as much physical information as possible.

The very high brightness of modern guns, combined with monochromators designs that preserve the brightness as much as possible, allow to perform q-resolved measurements with spatial resolution limited only by the Heisenberg principle. In other words, the spatial resolution is almost inversely proportional to the desired reciprocal space resolution. The later, in turn, should be determined by the maximum required spectral resolution, through the dispersion relation of the relevant excitation. It is thus likely that many applications of modern monochromators will arise from reciprocal space studies, where the physics is more straightforward and the resolution of the instrument will benefit from unblurred excitation analysis.

5. Lifetime measurements

It is tempting to believe that increased spectral resolution will lead to the possibility of measuring lifetimes of the excitations of interest. Indeed, as discussed at some length in

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Section 2, EELS (and CL) spectral resolutions are better than required for the measurement of some excitation lifetimes. In particular, the available ≈10 meV resolution is much smaller than typical linewidths of core-loss excitations (50–100 meV at least), or plasmons [37]. However, the physics behind the different decay channels can be quite difficult to identify, even in model cases such as $L_{2,3}$ edges where the peaks are well separated [38] (see also the discussion in Section 6).

In the optical domain, there is a particular case in which the link between linewidth and well-identified lifetime holds for surface plasmons [39]. The typical linewidths of these excitations are always above 100 meV, and they may be well isolated with respect to each other. In the case of simple structures not exhibiting complex spectra, the peaks measured in EELS are likely to be lorentzian (note that it is theoretically not always the case in CL, see [40]), and can be fitted with a well-understood model in which the lifetime is a parameter - note that it is thus not just a simple Fourier transform. In this case, the lifetime of the plasmon can be retrieved, but this cannot be easily extended to more complex situations in which, even in EELS, the spectra might not be lorentzian [41].

However, in the vast majority of cases, such analyses make very little sense, for various reasons. First, as discussed in the preceding sections, a given peak might be the signature of a sum of different excitations. This is the case for example for different surface plasmons of different, yet unresolved, q-momenta. This is also the case for physical systems in which electronic and positional degrees of freedom are intimately connected. For example, in molecules, each radiative state has a long lifetime, but appears as a broad peak in the spectra. The full width at half maximum extracted from a peak in the spectrum of such a system will therefore not be related to a meaningful lifetime - see e.g the case of quantum wells excitons [20]. To complicate matters, in many situations peaks or even bands from different excitations overlap, making the isolation of a given linewidth even harder. This is especially true in the case of EELS, which is an absorption/extinction technique as discussed in Section 3. Secondly, even assuming that one can isolate an individual transition in a spectrum, there is another reason for possible failure of lifetime measurements in spectral space. For core-loss excitations, the natural linewidths are not much smaller than 50 meV, and can thus now be resolved by EELS. However, in the case of low-energy excitations (optical, phonons...), the situation is quite different. As an example, the lifetime of the exciton dominating the optical spectrum of many systems of interest (quantum heterostructures, molecules...) is very roughly in the order of 1 ns. Assuming it appears at 1 eV (0.2 THz), this results in a rough estimation of the quality factor of the resonance to be $Q = E/\delta E \approx 2 * 10^5$. If we compare this value with the best results in the literature for EELS, namely from the Hermes machine conceived by O. L. Krivanek [7], we find a value of $Q \approx 100$ (10 meV at 1 eV). Note that the impressive performance of the Hermes machine is not to be blamed: a regular high resolution optical spectrometer will probably have the spectral resolution to resolve 1 ns lifetime (however probably not much more), but at the price of much reduced detection efficiency. Usually, such measurements are therefore made in the time domain directly.

Finally, the lifetime is often only one of the various types of information available from time-resolved experiments. For example, with ps resolution, acquisition of spectrum variations as a function of time can provide additional information, such as the charge carrier dynamics in semiconducting materials [42] or the local variation in the band gap in strained nano-objects [43].

Therefore, despite impressive achievements in the energy domain, the development of time-resolved techniques is certainly desirable in complement to high resolution spectroscopic techniques. In other words, the spectral and temporal experiments cannot generally be related through a naive Fourier transform analysis.

6. Enhanced stability and higher signal-to-noise ratios

In this section, we want to answer two questions:

- Why would we need an energy resolution much higher than the typical linewidth of given excitations?
- Provided we have access to high resolution (EELS, CL or SXES) spectrometers in a STEM, with which parameters can we play to get an optimised signal-to-noise ratio and therefore get the most from this high spectral resolution?

The first question finds its answer in the physics that we can probe with an enhanced resolution spectrometer. Once a given spectral feature has been identified as physically relevant/interpretable, most of the time the interest lies in the variation of the spectral features (energy position and linewidth, and more generally the exact shape of the spectra) as a function of some physical parameters. Obviously, this happens at sub-linewidth scales and therefore requires an enhanced spectral resolution. There is a plethora of examples. To name a few: plasmon energy and linewidth varies with local modifications of the dielectric environment (for example, hydrocarbon contamination [44]), plasmon linedwidth in non-crystalline samples depends on the grain size [45], exciton lines shift with charge environment (so-called “spectral diffusion”), excitons lines shapes change with excitation current [46], the linewidth of white lines forming $L_{2,3}$ edges depends on the exact environment of the metal atom in the crystal [38] ...

In Fig. 6, we show two examples of sub-linewidth features that are worth measuring to understand carbon nanotubes physics. In Fig. 6a, the difference in the carbon K-edge spectra for a metallic and a semiconducting nanotube appears as a shape modification of the spectrum. The same observation applies to Fig. 6b which shows the variation of the carbon K-edge due to a defect within the same carbon nanotube.

Therefore, high resolution spectrometry opens the way to a deep understanding of physical phenomena even if their related peak linewidths are broad; this will also be made obvious when discussing the interest of monitoring the temperature in Section 7.

The answer to the second question is multifold, however, most elements of this answer are deeply rooted in two important papers from O. L. Krivanek. One concerns the performances of EELS detectors [12], and the other the requirements *other than the sole aberration-correction capability* for building a useful aberration-corrected microscope [13]. We refer the reader to these essential texts. Here, we just illustrate how the absence of mechanical drift, of upmost importance in the prescription given by O. L. Krivanek in [13], impacts qualitatively the output of spectral-images (SI).

In Fig. 7, we compare plasmon mapping of the same silver nanocross performed on a modern microscope (NION USTEM 200) and an old one (VG HB 501). In both cases, the spectral resolution is around 270 meV (before deconvolution); the spatial sampling after binning is roughly the same, so is the EELS detection chain. The major difference is the absence of spatial drift in the USTEM that allows a significant increase in spatial sampling, in turn increasing the signal to noise ratio (SNR) to lead to reliable results, see Fig. 7. Of course, the spectral and spatial resolutions in Fig. 8 do not require any of the spectromicroscopes dealt with in this paper. Nevertheless, the ideas behind this example are easily translated to excitations with much smaller linewidth in much smaller objects: besides the energy and spectral resolution, a high mechanical stability is required in order to get the required SNR.

Another important aspect accompanying the development of monochromators is the overall energy stability improvement of

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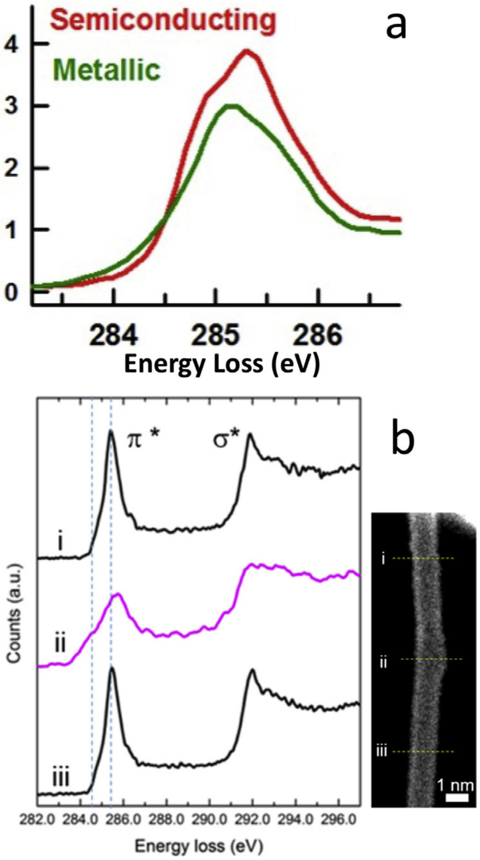

Fig. 6. Sub-linewidth spectral feature changes in carbon nanotubes. a. C1s spectra from a metallic and a semiconducting carbon nanotube. From [47], courtesy of G. Botton. b. C-K edges for a carbon nanotube presenting a defect acquired at three different positions indicated in the HAADF image on the right. From, [11], courtesy of K. Suenaga.

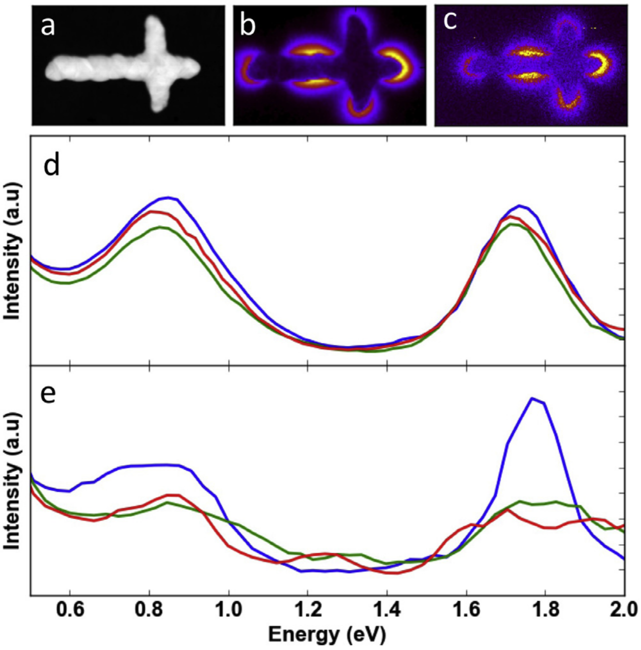

Fig. 7. Spectral improvement due to enhanced SNR. a. HAADF image of a silver nanocross (400× 250 nm). b. Filtered image (1.6 eV-1.8 eV) extracted from a ZLP-deconvoluted spectral-image acquired on a NION USTEM200 operated at 60 keV. c. Filtered image (1.6 eV-1.8 eV) extracted from a ZLP-deconvoluted spectral-image acquired on a VH HB501 operated at 60 keV. Both microscopes have the same nominal spectral resolution. The absence of mechanical drift in the NION however allows us to obtain an effective dwell time per pixel typically more than one order of magnitude larger than on the VG. b,c are qualitatively similar, but the noise is much higher in c. d: spectra extracted from the spectral-image in b. on three consecutive individual pixels close to the left tip. e: Same for the spectral-image in c. Huge variations in peak positions and widths are observed on the VG acquisition. The mechanical instability (drift) translates to a loss of spectral resolution. (data courtesy of P. Das and H. Lourenço-Martins).

the STEM-EELS instruments. In particular, the energy stability is strongly improved with respect to a non-monochromatised machine. For instance, dichroism experiments often imply several EELS measurements and post-processing of spectra, the results of which are very dependent on the exact position of the energy scale. Small energy drifts between measurements might easily give spurious dichroic results. Actually, the origins of magnetic or natural dichroism are Zeeman or Stark effects whose splitting is often of the order of a few tens of meV. Nevertheless, the dichroic signals can be measured quantitatively, even with only 300 meV energy resolution. However, the main condition is the energy stability, which should be of the order of a few tens of millivolts over long periods of time. This level of stability can also enable quantitative study of small physical energy shifts of EELS spectra. For instance, small changes in the energy barycenter of core-loss edges can be investigated and discussed in the context of charge transfer or charge accumulation [48], as exemplified in Fig. 8. In this example, electron density variations as small as 0.05 electron/unit cell could be measured in relation with energy shifts of the order of tens of meV in the Mn L-edge. Small electronic structure evolutions such as obtained from orbital re-arrangements (Jahn-Teller, strain-induced splitting, etc..), might also be detected by small energy shifts, even if the splitting cannot be directly observed in the EELS spectra due to lifetimes issues. The detection of such physical changes is also mostly a matter of energy stability and spectral SNR.

Another advantage of monochromatised STEM is the correction of aberrations at higher angles in the EELS spectrometer. This is required since energy resolution down to tens of meV has to be maintained using electron beams with convergence angles of severals tens of milliradians, as used in Cs-corrected machines. As a by-product advantage, the EELS fine structures become independent of the exact scattering conditions from the sample. One can thus safely attribute small EELS spectral changes observed when crossing interfaces between different materials to a physical effect and not to a change in the aberration contributions in the spectrometer. This is useful for measuring small energy shifts between materials but also for measuring dichroic signals, where spectra measured at different angles are compared.

We finally turn to the performance of the EELS detectors. Most of the ideas that are still driving the optimization of the EELS detectors can be found in the paper by O. L. Krivanek entitled “Parallel Detection Electron Spectrometer Using Quadrupole Lenses” [12]. This is a milestone paper for anyone interested in performing EELS experiments. The first part describes the electron optics of a simplified version of the high-selling Gatan PEELS system. The second part of the paper which is less-known, gives a broad panorama of the key features of a good EELS detector, specifically the optimisation of the detective quantum efficiency (DQE), and in which mode to operate it. It is striking that, thirty years later, most of the ideas are still perfectly pertinent to most modern detectors and should still be used as guiding rules in designing/using EELS systems. Of course, the field has progressed today, and an essential reference for the modern monochromator EELS performance characterisation was issued a decade ago by Lazar, Botton and Zandbergen [3]. In particular, the paper shows the role of the monochromation in cutting the ZLP spread, which can be more interesting than the gain in

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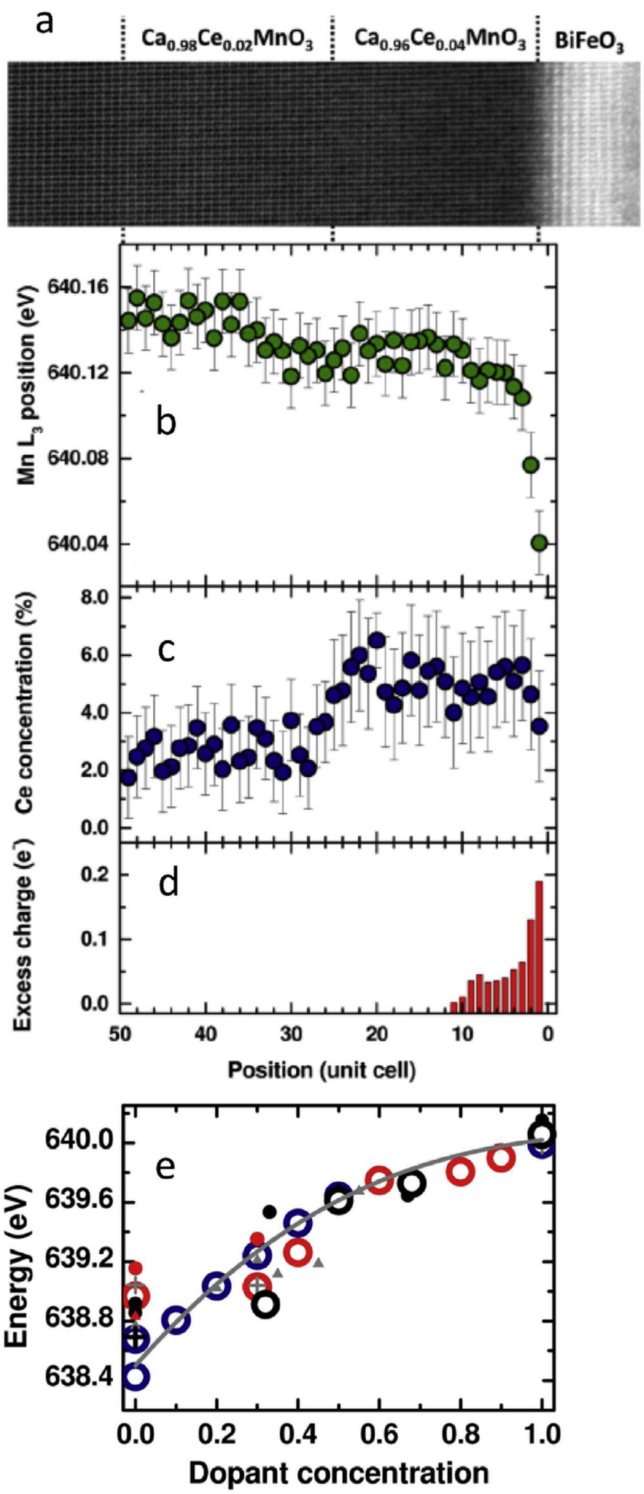

Fig. 8. Spectral improvement due to HT tank stability: excess charge determination in Ce-doped $CaMnO_3$ layers. a. HAADF image of the layers. b. Mn-L3 peak position extracted from EELS spectra unit cell by unit cell. c. Ce concentration profile for the same heterostructure. d. Excess charge per unit cell at the interface between the $Ca_{0.96}Ce_{0.04}MnO_3$ and the $BiFeO_3$, as derived from the relation in e. The error bars in panel b. and c. correspond to 80% confidence level. e. Relation between the Mn edge energy barycenter and the dopant concentration extracted from XAS data (see [48].) Adapted from [48].

spectral resolution for low-loss applications [49–53], with an emphasis on the need to improve the point spread function of the detector chain in that context.

For the next generation of EELS detectors, it is worth pointing out one remaining issue not discussed in the above-mentioned references: the presence of scintillator afterglow. It leads to phantom peaks in the EELS spectrum. Due to the high dynamics between the ZLP and any feature that one may want to see either in the low-loss or core-loss region, it can be one of the limits for the sensitivity (i.e, it will enter into the DQE as a time-dependent term in the gain variations). One way to overcome this limitation would be to use two dedicated detectors (dual-EELS), one of them dedicated to the ZLP measurement. Another possibility would be to use direct electron detectors with high dynamics, such as the one recently proposed for diffraction and imaging [54].

7. Low temperature and phase transitions

Up to now, we have commented on the type of excitations worth studying, on how improved spectral resolutions forced us to minutely consider the physical origin of spectra (absorption, luminescence...) or to work in reciprocal space. We also discussed the time-resolved approach. We have then discussed very general requirements to get the most out of higher spectral resolution.

Considering these points, it turns out that in the two main fields explored by O. J. Krivanek, high resolution imaging and high resolution EELS, we are probably settling at a limit. Much higher spatial resolutions than already achieved are probably not required, and much higher spectral resolutions seems to be difficult to achieve with foreseeable technologies. It is therefore certainly the time to widen the possibilities for studying materials by heavily relying on one of the basics concepts of solid-state physics: temperature. Indeed, it seems now essential to get a fine control of the temperature, and doing it would probably considerably widen the application range of high resolution spectroscopy in the TEM, as is standard in optical luminescence or synchrotron-based spectroscopic methods (XAS, resonant inelastic X-ray scattering -RIXS-, non-resonant inelastic X-ray scattering -NIXS- ...).

Below is a short compilation of reasons for controlling the temperature:

- Exploration of phase transitions. In this case, some precise spectral signature might be sensitive to various phase transitions, and its close monitoring as a function of temperature may reveal fine details in the transition. In particular, many metal-insulator transitions might be investigated, such as the one encountered for nickelate oxides (*RNiO*3 where *R* is a rare earth element) or vanadium oxide (V_2O_3, VO_2) [2]. While these transitions are well known in bulk material, they are less well known and poorly understood in nanostructures [55]. Also, some excitations may simply not exist above a given transition temperature, therefore temperature control is often a prerequisite for assigning low-energy features to specific excitations (excitons, phonons, magnons...).
- More generally, the temperature dependence of an excitation might be the signature of peculiar electronic structure features. A well-known example is the temperature dependence of exciton line intensities in confined semiconductors. The absence of intensity variation as a function of the temperature is usually considered as a strong evidence of three-dimensional confinement.
- Enhancement of signal. Temperature might be a cause of linewidth broadening; as the resolution is now of the order of 10 meV in EELS (and much less in CL), this is certainly an effect that can limit the sharpness of peaks at room temperature ($k_bT_{room} = 25$ meV). However, there exist less obvious ef-

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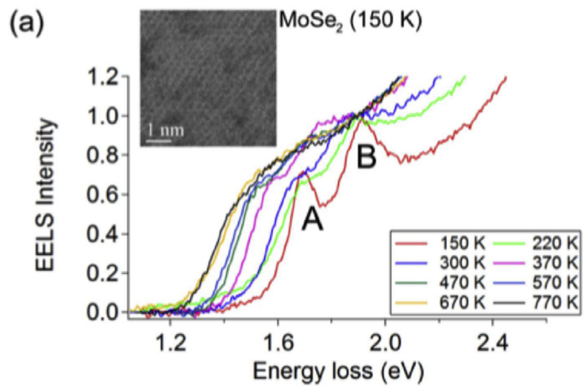

Fig. 9. Effect of the temperature on the visibility and energy position of the excitonic lines in EELS, here illustrated in the case of an *MoSe*$_2$ monolayer. Courtesy of L. H. G. Tizei, reprinted with permission after [56].

fects that may influence the quality of the spectra and therefore the conclusions that can be drawn concerning the physical properties of a material. In correlated-fermions systems, such as electrons in a solid, some excitations of relatively high energy with respect to temperature might still be strongly influenced by the temperature. For example, in the case of excitons (see Fig. 9), the binding energy E_b that is far smaller than the energy-difference between the electron and hole. As the temperature is raised above the equivalent temperature E_b/k_bT, the electron-hole pair get ionised, and the spectral shape is considerably blurred.

- Finally, a considerable range of irradiation-sensitive materials, which certainly have spectral features requiring a high spectral resolution (molecular lines for example), would benefit from cooling.

8. Electron beam manipulation

It is obvious that a wide range of experiments using the exciting new types of instrumentation discussed here are being or will be performed in the near future. However, we haven't much discussed possible new technological developments that have been arising in parallel to the improvements in energy resolution in the past twenty years. Fig. 10 is an attempt to classify broad and somewhat arbitrary categories of physical phenomena (left column in Fig. 10). These are:

- Bulk properties of non-correlated materials: basically everything that can be described in a band structure approach for an infinite solid (core excitations, phonons, interband transitions, ...), simple excitations resulting from interactions between single particles in an infinite (excitons, bulk plasmons, phonons...) or semi-infinite solid (interface plasmons). These correspond to the historical use of EELS, CL and EDS/WDS/SXES in TEM and scanning electron microscope (SEM), with the notable exception of low-energy excitations such as phonons.
- Many-body effects: these correspond to any effect that cannot be trivially understood in a single particle framework, and encompass ferromagnetism and ferroelectricity, metal-insulator transitions, etc...
- Classical confinement: this covers any classical electromagnetic excitation (surface plasmon, polaritons, surface phonons...) that gets modified when the boundary conditions of the subtending particle are modified - localised plasmons and phonons, guided modes... .
- Quantum confinement: this covers any quantum excitation that can be spatially confined, essentially electron-hole pairs and excitons.
- Quantum optics: this covers any problem where the quantum phase of an object is of importance, as in the case of quantum bits or single photon emission.

All these broad categories of problems have been addressed by describing the incoming electron essentially as a classical particle, or, at least, a quantum wave for which only the amplitude (and not the phase) is important, as in the case of atomic incoherent imaging [65].

However, the electron beam possesses other properties that are increasingly being used, and which may be better adapted to addressing specific physical problems. These are:

- Time-resolution. Pulsed-electron guns have been used for a long time for lifetime measurements of bulk and quantum-confined semiconducting systems [66]. We have already discussed the interest of such an approach in unveiling physical effects, but we could also add its interest for the study of optical non-linear effects [67]. Pulsed guns have also been used to perform electron energy-gain [68] experiments on large nanoparticles [59], or confined-plasmon materials. In these cases, what is learned about the material is not obvious (in particular because the lifetimes of the excitations involved are much shorter than the electron pulses [37,69]). On the other hand, the gain in understanding about the electron/matter/photon field interaction is amazing. To our knowledge, pulsed-guns have not yet been used to gain information from many-body systems, although it is common-place in other spectroscopies like e.g. angle-resolved photoemission spectroscopy (ARPES).
- Phase-shaping: manipulating the phase of the incoming/outgoing electrons in conjunction with spectroscopy has been sparsely used. However, using the incoming electron phase symmetry for understanding material symmetries is quite interesting [70]. In solid state physics, EMCD [62] and other flavours of dichroic-like techniques induced by the disruptive use of phase-shaped beams [70] are starting to be used. The chase for increased stability should probably help for example in gaining enhanced dichroic signals, see Section 6. Holographic methods for the exploration of surface plasmons have been reported [61]. A very recent application of beam-shaping has been shown for the exploration of classical confinement [63], where the phase of the incoming beam is shaped so as to match different plasmon symmetries, exciting or not plasmon resonances. We are not aware of applications of shaped-beam or holography experiments for quantum confinement or quantum optics applications.
- Finally, a very special use of pulsed guns has recently enabled the incoming electron beam to be put into a coherent superposition of states of different energies (thereby creating a non-stationary state of free electrons) [64]. In this way, Rabi oscillations of the free electrons could be measured. It is not clear at the moment if this approach could be of interest for spectroscopy in the STEM. However, it is sure that it will develop as a full branch of electron microscopy by itself ("quantum-coherent electron microscopy").

The combination of these different flavours of electron beams with ultra-high resolution spectroscopy is still to be realised. Quite surely, it would help in gaining new insight into the physics of nano-objects.

9. Conclusions

In this paper, we have tried to review several considerations related to the best usage of new-generation spectromicroscopes. Al-

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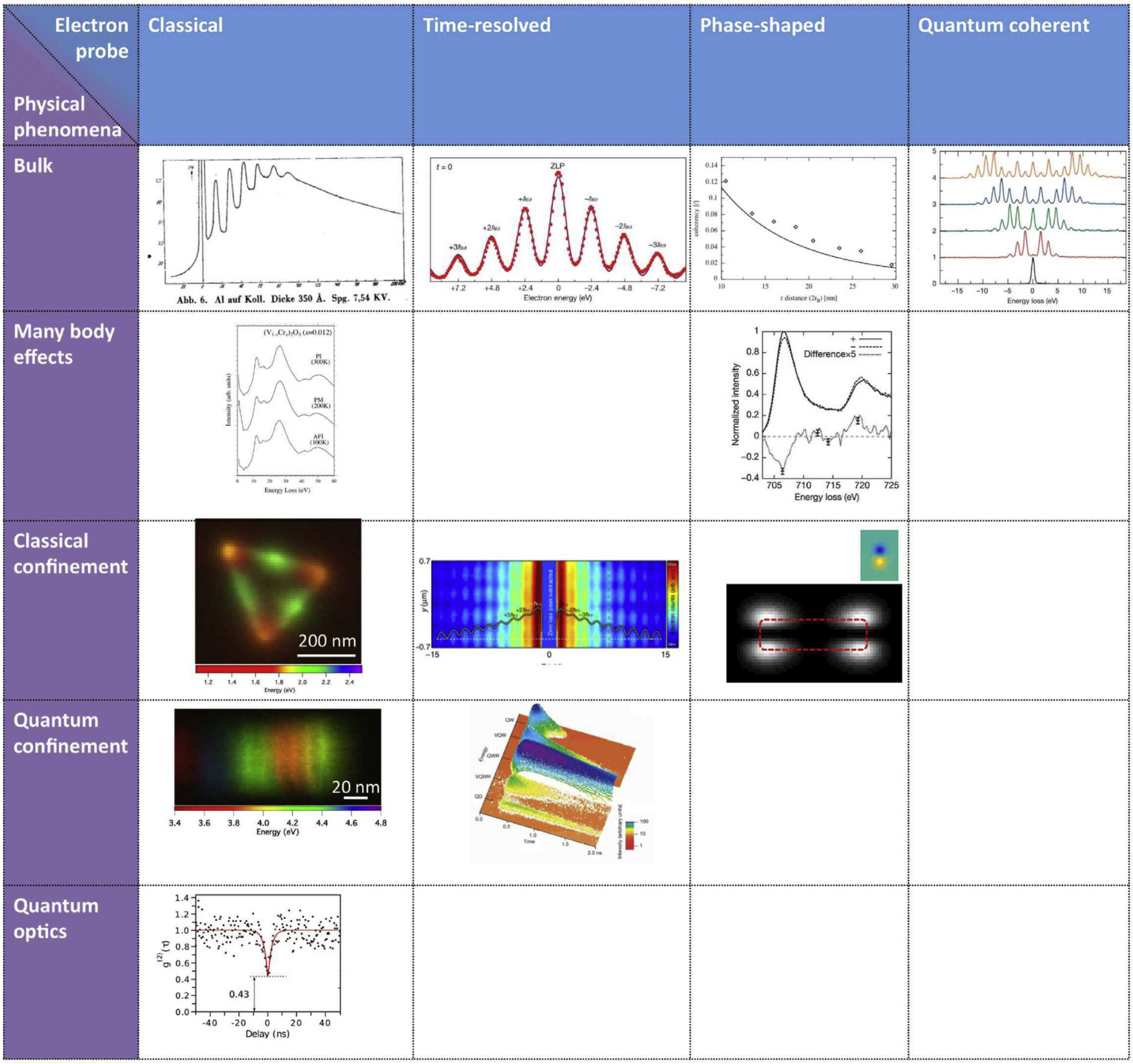

Fig. 10. Summary of different physical phenomena ("Physical phenomena", rows) and how they can be tackled with electron spectroscopy techniques using different forms of electron probes ("Electron probes", columns). Bulk/Classical: EELS spectrum of (multiple) plasmons in aluminium foils, from [57]. Many body/Classical: Low-loss spectrum of $(V_{1-x}Cr_x)_2O_3$ (x=0.012) measured in three temperature-dependent phases. From [2], reprinted with permission. Classical confinement/Classical: Plasmon mapping on a silver triangle. Adapted from [22]. Quantum confinement/Classical: GaN quantum discs mapping by cathodoluminescence. Adapted from [20]. Quantum optics/Classical: Time-correlation function from a single point defect in hexagonal boron nitride, exhibiting a dip as is typical for single photon emission. Adapted from [58]. Bulk/Time-resolved: Electron-Energy-Gain (EEG) Spectrum. From [59], reprinted with permissions. Classical confinement/Time-pulsed: EEG spectrum on a plasmonic resonator. From [60], reprinted with permission. Quantum confinement/Time-resolved: Time-evolution of the emission of quantum emitters in cathodoluminescence. From [42], reprinted with permission. Bulk/Phase-shaped: Bulk plasmon spatial coherency for Al. From [61], reprint with permission. Many-Body effects/Phase. Experimental dichroic signal in EMCD on the Fe $L_{2,3}$ edges for 10 nm Fe on GaAs. From [62], reprinted with permission. Classical confinement/Phase-shaped: Mapping of the dipolar mode of a dipolar plasmon within an Al rod using a *pi* beam (inset). From [63]. Bulk/Quantum coherent: Signature of Rabi oscillations of the electron beam as observed on the EELS/EEGS signal. From [64], reprinted with permission.

ready, many new results taking advantage of the high spatial and spectral resolutions have come out. We hope that some of the lines of inquiry described in this paper will help to get the best out of these exceptional instruments.

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