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From a physicist's toy to an indispensable analytical tool in many fields of science

A personal view of the leading contribution of Ondrej Krivanek to the spectacular successes of EELS spectroscopy in the electron microscope

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ABSTRACT

This contribution aims at reporting, from the subjective point of view of a witness based in Orsay, the fundamental role of Ondrej Krivanek in the spectacular emergence of EELS (Electron Energy-Loss Spectroscopy) as a key tool in analytical electron microscopy. In this regard, he has successively designed and built while he was at Gatan, serial EELS spectrometers, parallel EELS spectrometers and post-column energy filters which have been fitted to many different (S)TEM columns installed around the world. More recently the implementation of monochromators on the NION dedicated STEM together with the realization and performance of aberration correctors (which lie out of the scope of the present review), have placed the most advanced instrumental tool in the hands of continuously increasing populations of users in many domains of materials science and in life sciences. Furthermore, the impact of Ondrej Krivanek has spread widely beyond his technical achievements into that of a highly respected organizer of workshops, bringing together at regular intervals, all the experts from around the world and building up a real community of scientists.

1. Introduction

One day, at the end of July 1978, Ondrej Krivanek and myself first met, during a specialist workshop in Analytical Electron Microscopy (AEM), held at Cornell University. This was the second workshop of this name; the first one two years earlier, had beautifully introduced and promoted the general concept and the practical aspects of AEM. In this context, spectroscopy tools added onto the column of a transmission electron microscope (TEM) constitute useful components which enlarge its domain of exploration by providing local information on the chemistry as well as on the electronic properties of the specimen. By the way, two papers published a couple of years before in the first issue of the journal Ultramicroscopy had firmly established the fundamentals and the perspectives of the EELS technique in a TEM. The first one by Isaacson and Johnson [1] had focused on the use of EELS for the microanalysis of light elements, evaluating the two important parameters to be improved, the Minimum Detectable Mass (MDM) and the Minimum Detectable Mass Fraction (MMF), and concluding after a first round of preliminary experiments that "the feasibility of elemental analysis of single light atoms remains a distinct possibility (in theory, at least!)". On their side, Colliex et al. [2] had more extensively described the richness of the information contained in an EELS spectrum recorded in the transmission mode from a nm-sized area and revisited the influence of various parameters in the drive towards the ultimate detection limits using this technique. I however confess that the use of the word "ancillary" in the first sentence of the conclusion of this paper "Electron energy loss spectroscopy must be regarded as a very promising ancillary method in electron microscopy", does not sound today very optimistic, when reading it!! I want to point out at this stage, that both papers were mentioning the development and introduction of parallel detection devices as an anticipated necessary step to come closer to the identification of the individual atom.

It is therefore no surprise that the EELS technique was in 1978 at the center of heated debates concerning the future of AEM. Therefore, the young Ondrej Krivanek came to me and asked: "Christian what do you think of the future of EELS?". Listening to his own report of the ensuing exchange, it now appears that I did not show a great deal of optimism, diverting the discussion toward other subjects (liquid metal ion sources, contrast of inelastic images of phase objects…) which I was exploring at the same time with my first students, Pierre Sudraud and Claudie Mory. I feel that I may have masked a bit that a third student, Pierre Trebbia, was very much involved at that time in the introduction and use of computer control and analysis to progress towards quantitative processing of EELS data. Revisiting now my own blurred

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memories, maybe I had felt that if such a young and bright guy, Ondrej, had immediately entered this field, the competition would quickly have become very severe. You all know, now, what happened: the rest of this paper will emphasize the major inputs, realizations and successes in the field of EELS in a (S)TEM, which have to be unambiguously attributed to Ondrej Krivanek and which the many different contributions to the present Ultramicroscopy issue beautifully illustrate today, i.e. 40 years after the beginning of my story here above. I can also recommend to interested readers the TEM-EELS personal perspective by Ray Egerton, published a few years ago in a previous issue of Ultramicroscopy [3].

2. The first generation of Gatan serial EELS

As a matter of fact, the sixties and early seventies had been rich with instrumental developments of energy analyzers and filters (magnetic sectors, combined magnetic sectors-electrostatic mirrors, Wien filters) either introduced in the middle or at the bottom of the TEM column. These systems, all made through local initiatives in research laboratories (Chicago, Orsay, Oxford, Cambridge, Cornell), had generated an initial output of fundamental physical studies, such as the excitation spectra of nucleic acid bases [4,5], the fine structures on core losses in different materials including solidified rare gases [6,7], the dispersion curves E(k) of plasmons and Cerenkov losses [8] in thin metallic and semiconducting films. But, it could be pointed out that no such attachment was commercially available for TEMs, except a first design of an EELS magnetic sector on top (i.e. at the end of the electron trajectories) of the newly built VG HB5 dedicated STEM microscope, the first versions of which had been installed in London and Cambridge in the mid 70 s. Obviously, this domain constituted at that time a potentially rich market.

Let us come back to Ondrej's start in EELS in 1978 after the Cornell workshop, a description of which can be found in his own account published in the Proceedings of the IFSM meeting in Prague 2014 [9], when he was awarded the IFSM Cosslett medal. Back at the Lawrence Berkeley National Lab where he was employed at that time, he convinced his boss, Gareth Thomas, to give him the modest support required to build his first spectrometer described in an EMSA abstract in 1979, and producing spectra over large energy ranges (from zero to 2000 eV) at about 2 eV resolution, see Fig. 3 in [9]. This was quite an encouraging achievement. He was quickly approached by Peter Swann, head of the young Gatan enterprise, and they designed together the mark II, which became the Gatan 607 serial EELS, described in [10]. By this time, he had moved to ASU as Associate Director of the HREM facility, where Fig. 1 shows him at work in his office and outside in the Arizona environment. His long and fruitful connection with the Gatan company had started in parallel, where he later became Director of Research.

The year 1981 was particularly rich in results issuing from ASU, with four papers at the EMSA meeting and one at the EMAG conference, and also from Orsay with three papers at the EMAG conference. The work performed at ASU was mainly focused on the retrieval of crystallographic information and on the role of orientation, giving rise to channeling and blocking effects. It also resulted a little later in the famous EELS Atlas, the reference guide of electron energy loss spectra covering all stable elements, jointly published by ASU HREM Facility and Gatan Inc. [11]. I can testify that I have myself been an addict of this Atlas which was always accessible on the microscope control table while I was recording spectra.

Ondrej came and spent three months in Orsay during spring 1981. We had acquired a few months earlier one of the first HB 501 dedicated STEM VG microscopes and we were on the verge of pushing this bright new machine into the exploration of its analytical performance capacities, the first of which was obviously that associated with EELS spectroscopy. Ondrej had brought a prototype of the EELS 607 spectrometer, which immediately demonstrated much higher performance than the original VG spectrometer [12] and this became our work instrument until it was sent to retirement with the arrival of the second generation of Gatan spectrometers, i.e. the parallel detection system. As a matter of fact, the 607 serial Gatan spectrometer benefited from an efficient correction second order aberrations due to an improved design of its pole pieces as well as a better optical coupling, leading to better transmissivity. At this time, with a probe of 0.5 nm, the signal-to-noise ratio was sufficiently good to record core-loss spectra (i.e. Ca L_{23}) with a 1 eV energy resolution, while the FWHM of the zero loss peak was of the order of 0.4 eV. Early applications involved spectra and energy-filtered images of uranium clusters on thin foils of carbon and of Si-SiO_2 interfaces [13]. Through these studies, the association of a STEM fitted with a field emission gun (FEG) of high brightness capable of delivering a current of a few pA to hundreds of pA in a sub-nm probe, with a suitably adapted and corrected EELS spectrometer, had clearly been demonstrated to constitute an excellent way of exploring the use of electron spectroscopy in materials with the best performance then available.

Let us move to the year 1988, when Mike Isaacson and myself managed to obtain from our agencies, NSF in the USA and CNRS in France, the financial support for the organization of a workshop at Aussois in the French Alps during winter, which would be “in effect” a third Cornell meeting, ten years after the second one. This new workshop, devoted to “nanometer-scale electron microscopy”, provided an evaluation of the progress and successes obtained over the previous decade, mostly but not uniquely when applied to materials science. The proceedings of this workshop, gathered in a single Ultramicroscopy issue [14] are very rich in illuminating contributions, interlaced with summaries and conclusions. As regards EELS in the (S)TEM, the focus at that time was on detection systems and more particularly on parallel EELS. It was not a surprise, as such an upgrade had been firmly recommended more than ten years before [1,2]. As noted by A. Eades [15] in his summary of the session on one- and two- dimensional electron detectors encompassing the description and discussion of six parallel EELS detection systems, “the revolution observed in electron detection is brought in part by the development and incorporation into electron microscopy of CCDs and PDAs, and in part by the advances in computing and digital storage, that have made it possible to acquire and process large numbers of images in digital format”. In his own contribution to this workshop proceedings, Krivanek describes improvements which he has brought to the Gatan parallel EELS spectrometer under development [16]. Fig. 2, recorded during this meeting, shows the high density of (S)TEM-EELS experts gathered in the sunny French Alps, where our ski champion, Ondrej Krivanek, keen to mention in his wikipedia list of awards his “1st places in special and parallel slaloms at the 1975 Oxford-Cambridge Varsity ski race”, could fully demonstrate his skills on the steep slopes.

3. The Gatan parallel EELS system and the subsequent EELS spectrum-imaging era

As a matter of fact, the presentations on parallel EELS detection in Aussois stemmed from a flourishing context of previous studies. As early as in 1981, with the target of pushing down the detection limit for a trace element (typically Ca) in a biological tissue, Shuman had tested the implementation, pros and cons, of photodiode arrays either under direct electron exposure or with the introduction of light-conversion systems [17]. Using a light-coupling design together with a multiple-element photon detector, Shuman together with Kruit [18], then with Somlyo [19], developed the necessary routine to process the so-acquired low signal-to-background spectra and to extract quantitative measurements of weak concentrations. On their own side, Krivanek and colleagues at Gatan [20], had also undertaken the installation and test of a parallel detection system, made of a three-quadrupole magnification unit delivering variable ranges of energy-loss electron distributions on the parallel EELS detector. This latter was made of a

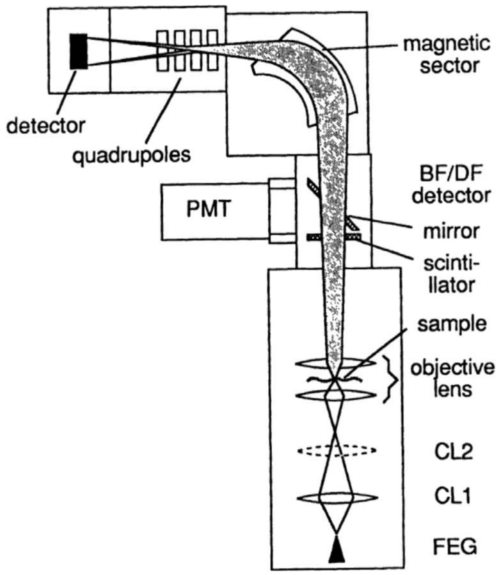
Fig. 1. Ondrej Krivanek in his early days dedicated to developments in EELS, while he was acting as Associate Director of the NSF-funded HREM facility at Arizona State University: (left) in his office in 1985 during the 100th year of ASU celebration meeting dedicated to High Resolution Electron Microscopy; (right) practicing western style.

YAG scintillator fiber-optically coupled with a cooled photodiode array. In the following years, this device benefited from improvements (such as those described during the Aussois meeting in 1988 [16]) and was even tested on the VG HB501 STEM installed at IBM San Jose.

To further evaluate this type of combination, Ondrej Krivanek came again to Orsay early 1990 for a longer six-month period with a newly developed Gatan 666 PEELS spectrometer. Fig. 3 shows a schematic diagram of this spectrometer mounted on the FEG-STEM together with an image testifying that the spectrometer and its post-spectrometer quadrupole coupling are still in operation on top of our machine 25 years after first installation. The only change in this image with respect to the original configuration consists in the new generation of dual EELS detector locally developed by Marcel Tencé, under test when this picture was recorded a couple of years ago. The machine was immediately used for addressing some issues related to the atomic-level microstructure of inorganic solids: clusters of a few atoms or isolated defects [21]. In a series of EELS analyses realized on individual clusters made of a few thorium atoms deposited on very thin carbon films, Krivanek et al. [22] pushed the analysis of difference-spectra as far as the quantification of numbers of atoms down to the level of "quasi" single atoms. These results were quite similar to those obtained by Leapman and Hunt at the same time [23]. It must be added that the identification of single atoms with this technique was unambiguously demonstrated on peapods incorporating single rare earth atoms, only in the year 2000 [24].

During the Aussois meeting, another contribution by Jeanguillaume and myself [25] raised a high level of interest, the introduction of the spectrum-image concept, which could be applied to any type of spatially-resolved spectroscopy. As a matter of fact, the access to parallel spectroscopy and to the associated fast acquisition rate of

Fig. 2. Group photo recorded during the NSF/CNRS workshop on "Electron beam_induced spectroscopies with high spatial resolution" in Aussois, France (March 1988), in which Ondrej Krivanek is surrounded by most of the major actors in the field of Analytical Electron Microscopy at this time.



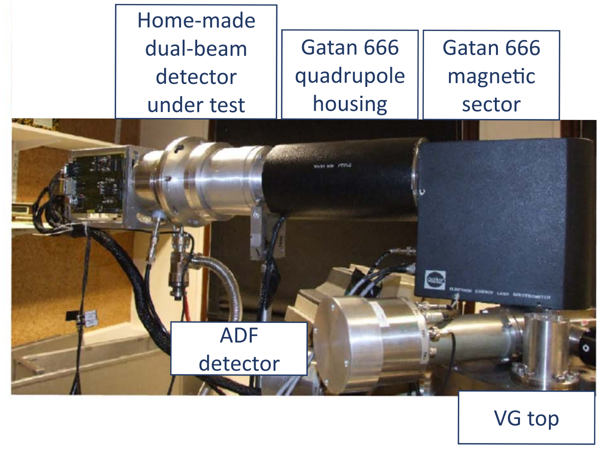


Fig. 3. The Gatan 666 PEELS spectrometer mounted on top of a VG STEM column: (left) schematic and (right) present view of the magnetic sector and quadrupole lens coupling still in daily operation, while the detector itself is a home-made dualtype detector.

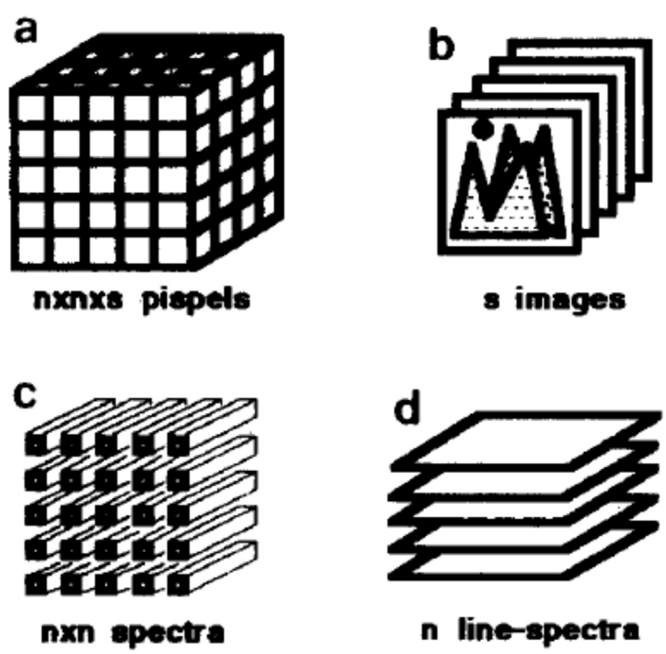


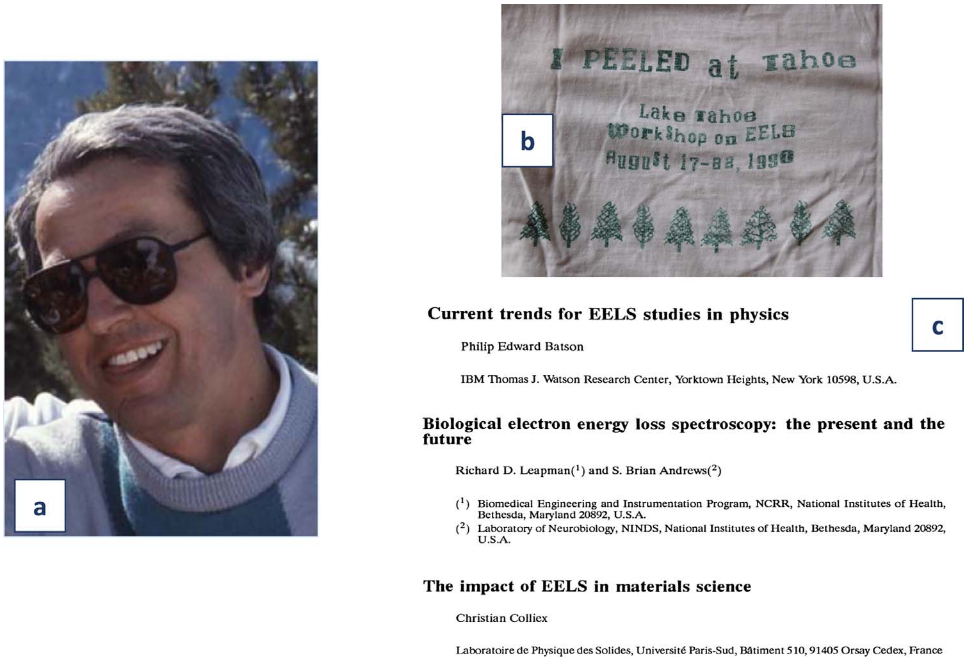
Fig. 4. Definition of the spectrum-image data cube (a) and of the elementary objects resulting from its sections (from [25]).

EELS spectra was crucial for recording large numbers of spectra covering a substantial area of the specimen under investigation. As shown in Fig. 4 (extracted from [25]), several different acquisition modes are available for the acquisition and storage of these 3D volumes of data. And the conclusion of the paper was a confident message of belief in a widespread adoption of the technique, stating “that the first results will start appearing in the near future”. The first generalized spectrum-imaging implementation in electron microscopy essentially dedicated at that time to the production of elemental maps, was described by Hunt and Williams [26]. It includes the description of the software necessary to disentangle some of the problems raised by the processing of large amounts of data, possibly associated with drifts in space and energy. At the same time, Balossier et al. [27] described how to introduce the difference methods in a spectrum-image, associating for the same image pixel an EELS spectrum, a dark field and a shield current. A review of the possibilities of spectrum-image acquisition, processing and applications in very different situations from inorganic multilayers to unstained T4 phages was then published by the Orsay group [28]. In this paper, mapping different types of bonds or detecting transient phenomena through the associated fine structures on the recorded edges was demonstrated. One knows how generally this technique is used nowadays.

In the definition of spectrum-images, it was pointed out that the data could be stored either in a STEM approach where extended spectra were acquired point by point when scanning the incident probe on the specimen, or by sequentially recording collections of images filtered through a slit of finite size corresponding to different energy windows. This approach is known as Energy Filtering TEM (EFTEM) or Electron Spectroscopic Imaging (ESI) and methods for extracting chemical maps from such datasets were developed by Lavergne et al. [29] The interest of inserting at the bottom of a TEM a high-performance filter had not escaped the attention of Krivanek. In this period he designed, constructed and tested a post-column imaging filter that could be attached to most standard TEMs (operated at voltages up to 400 kV) demonstrating excellent properties in imaging and in spectroscopy [30]. I have not followed myself this adventure and will not describe it any further here. I only point out that Ondrej's publication list mentions nearly 20 presentations or publications on energy filtering over the period 1992–1995, most of them cosigned by Sander Gubbens.

4. Ondrej Krivanek as a prominent workshop organizer from 1990 Tahoe EELSI to 2013 Sainte Maxime EDGE

In the meantime, Ondrej revealed himself as a top-level workshop organizer. EELS having definitely emerged as a rich source of analytical and more generally of spectroscopic signals in the electron microscope, a dedicated workshop would be the ideal place to compare projects, to recount successes, to identify limitations and to stimulate novel aspects of research. Consequently, a first workshop of this type dedicated to Electron Energy-Loss Spectroscopy was held in August 1990 (i.e. two years after the Aussois meeting) at Lake Tahoe in California, immediately following the International Conference on Electron Microscopy ICEM 12 at Seattle. This workshop, named EELSI at that time, was organized by Ondrej Krivanek and wholly sponsored by Gatan Inc. It benefited from the creative suggestions of the scientific committee gathered around Ondrej and consisting of Phil Batson Ray Egerton, Mike Kundmann, Richard Leapman and Peter Rez. It took place in a



Current trends for EELS studies in physics

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Biological electron energy loss spectroscopy: the present and the future

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The impact of EELS in materials science

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Fig. 5. Lake Tahoe workshop on Electron Energy_Loss Spectroscopy (1990): (a) the chief organizer Ondrej Krivanek; (b) the logo tagged on every-one's tee-shirt; (c) the three summaries and comments at the end of the proceedings published as a special issue of Microscopy, Microanalysis, Microstructures [31].

very relaxing and stimulating environment (see Fig. 5) and it attracted the most expert international platform of researchers at that time. The Proceedings of the workshop [31] contain a remarkably rich collection of contributions on basic aspects of the near-edge and low-loss EELS structures, as well as developments in the quantification of the data and reports on the most relevant progress in instrumentation and techniques at that time. Some of them have been referred to above in the present text [22,23]. Of specific interest for those concerned today by the historical development of the technique and its successes in the exploration of new fields in physics, biology and materials science, one can also quote the three summaries gathered at the end of these proceedings (Fig. 5).

In the aftermath of this first meeting, Ondrej became quickly convinced that it should be transformed into a repeated event. Through his continuing efforts a succession of workshops organized in the same spirit have taken place every four years, the next one (EDGE 2017) being planned for May 2017 and organized by our Japanese colleagues in Okinawa island. Many of us can therefore remember all of these successful and superbly enriching meetings which moved our community from Leukerbad, Switzerland (EELSI 1994) in July 1994, to Port Ludlow, USA (TARA 98) in September 1998, then to Guadeloupe, France, West Indies (SALSA 2002) in May 2002, to Grundlsee, Austria (EDGE 2005) in May 2005, to Banff, Canada (EDGE 2009) in May 2009, to Sainte Maxime, France (EDGE 2013) in May 2013. They have all been real successes, regularly attracting over 100 participants (as can be seen in Fig. 6) from all over the world and more and more from connected fields (theory, photon beam spectroscopies and others). Ondrej has been quite very active in the scientific, if not in some aspects of the local organization, throughout these 25 years. I am pretty sure that EDGE 2017 will be a new success along these same lines, that were originally drawn by Ondrej.

5. The most recent successes: the combination of aberration correction and EELS monochromatization

Let us move quickly now to the most recent years, over which period I have not been in direct connection with him and cannot therefore testify. As everybody knows however, he has devoted all his energy starting around 1995 to the realization of an innovative generation of aberration correctors for STEM microscopes, bringing the point resolution of these instruments into the sub-Angström range. He also left Gatan and after an enriching period at the Cavendish in Cambridge, he created, together with Niklas Dellby the company NION.

This company produces a brand new generation of dedicated STEM instruments from gun to detectors which can routinely deliver maps of EELS-generated information (elemental analysis, electronic state) with an atomic level resolution, as has been demonstrated in so many papers over the past five years. On this side, I have only been a customer, signing an order for a 200 kV Nion UltraSTEM, which was fully installed in our laboratory in 2011 and since then has produced excellent results in many different domains of materials science (defects, interfaces, multilayers, graphene and associated 2D materials like BN, dichalcogenides, ...) [32]. I confess that I am no longer myself a user of the machine, but all my colleagues here at Orsay are very keen users of it and we have even placed an order for a second machine, called HERMES, which combines the aberration corrector with a monochromator.

I will therefore conclude this historical review with some words about the design and construction of a monochromator specifically dedicated to an aberration-corrected STEM column, thereby combining on a single machine the best performance in terms of spatial and energy resolution. Fig. 7a shows a schematic diagram, extracted from Ondrej's paper in the Lake Tahoe Proceedings [33], representing an EELS apparatus using only magnetic elements for the monochromator and the filter, which "should" be capable of attaining an energy resolution of a few meV at primary energies of 200 keV. When considering this scheme, I wish to draw attention to two details: (i) the energy selection in the monochromator is realized by a slit, the two blades of which being insulated so that the current falling on each of them can be compared and a stabilizing feed-back can be set on the high voltage to maintain the beam precisely centered on the slit; (ii) the two magnetic filters are connected in series so that the instabilities in the high voltage or the filter current do not result in a loss of energy resolution. When referring to the most recent publications of the NION team describing the design [34], and the realization and performance demonstration of their high-resolution monochromator [35], it is quite

Fig. 6. EDGE (Enhanced Data Generated by Electrons) at Sainte Maxime, France (2013), the latest workshop in the series initiated at Lake Tahoe more than 20 years before. The group picture demonstrates the permanent ability of these meetings to attract participants from around the world and of all ages. Inset: Ondrej Krivanek still acting as one of the scientific committee members.

interesting to point out how the recommendations put forward twenty years before have been practically satisfied so that the predicted results have been achieved. As predicted previously, these results open broad completely unexplored fields of research, in particular in the very low energy-loss range, where phonon or molecular vibrations can be studied at an unprecedented level of spatial resolution [36]. As an example, Fig. 8 compares a spectrum recorded in the early seventies by Isaacson [5] on a nucleic acid specimen showing the electronic excitation spectrum from UV to far UV compared with a very recent spectrum recorded with the Hermes machine at ASU [37] in the aloof mode on a guanine thin crystal. Here the spectrum fully covers the IR spectral window and agrees very well with a reference IR optical spectrum. We can conclude that it fully answers one of the recommendations put forward by Isaacson and Colliex at the end of the Aussois meeting [38]: “Develop low-energy spread electron sources or imaging monochromators for energy resolution in the 10 s of meV regime in combination with high spatial resolution”.

6. Conclusion

The present contribution had a limited scope, i.e. to deliver a personal account on a subject and not to write down a comprehensive

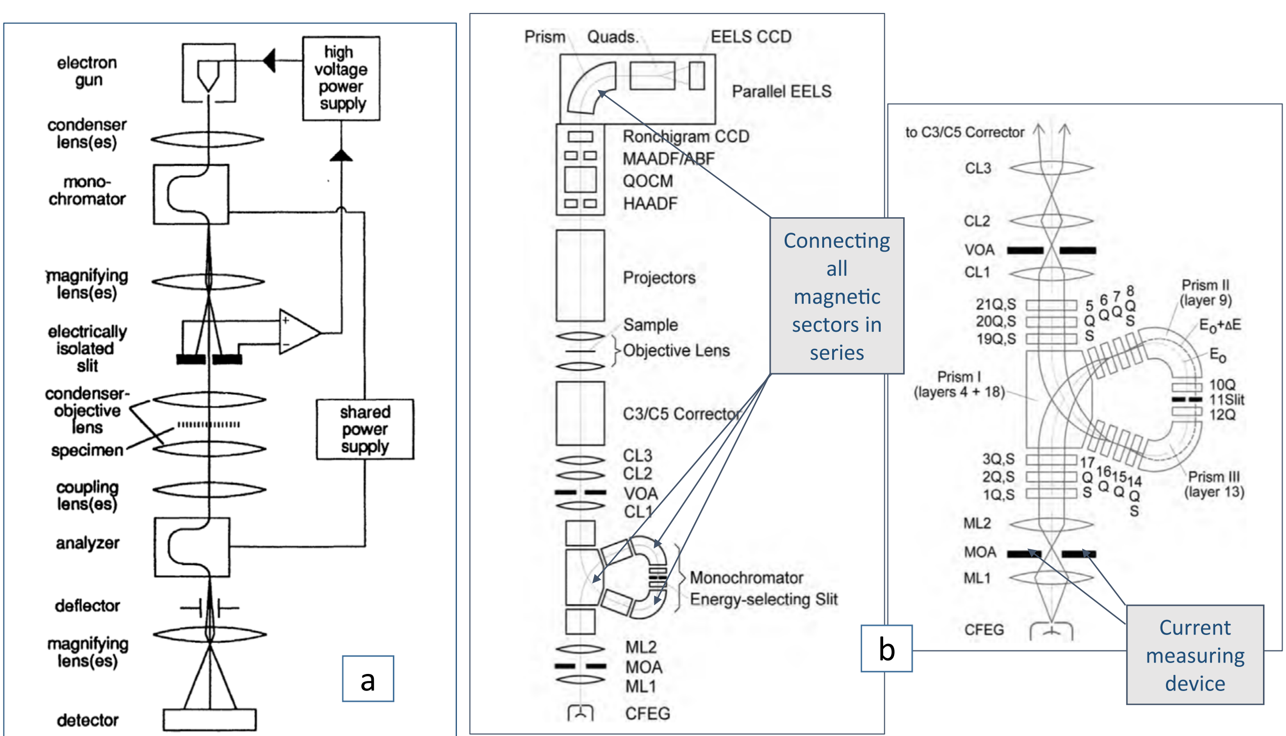

Fig. 7. Design of the STEM with monochromator; (a) as conceived in the Lake Tahoe contribution in 1990 [33] and (b) as it now in the NION Hermes instrument about 25 years later. Note the implementation on the present version of key connections and measuring devices, suggested in [33], which now give access to the 10 meV energy resolution domain ([35–37]).

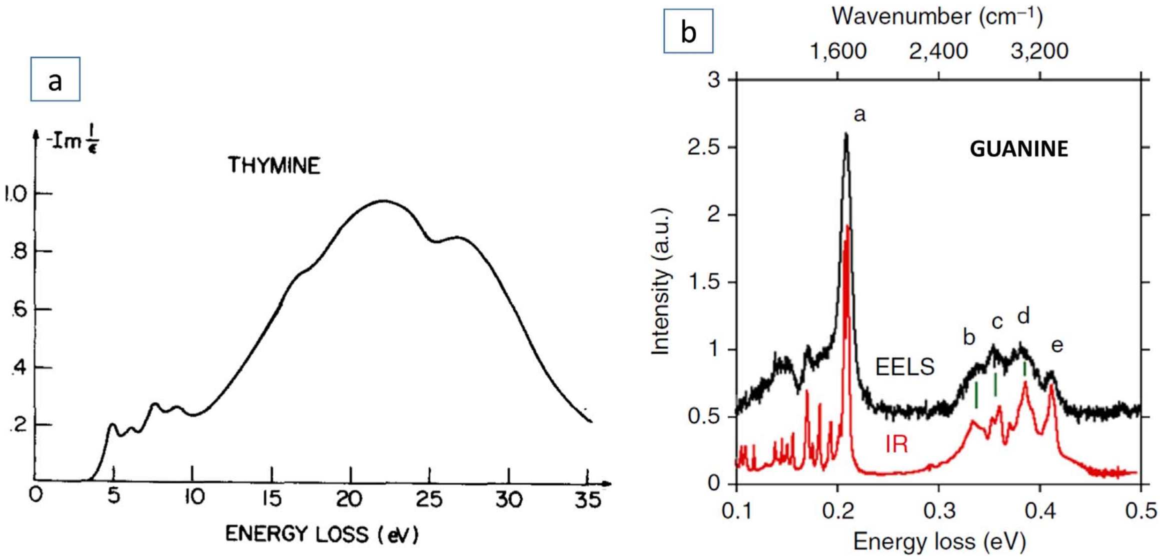

Fig. 8. Comparison of top-level EELS spectra recorded on nucleic acid bases respectively in 1971 [5] and in 2016 [37]. The first one covers the UV-far UV range, i.e. typically from 3 to 40 eV with a 0.5 eV resolution while the second one, compared to a pure optical IR spectrum, exhibits the most important features between 0.1 and 0.5 eV with around 10 meV resolution.

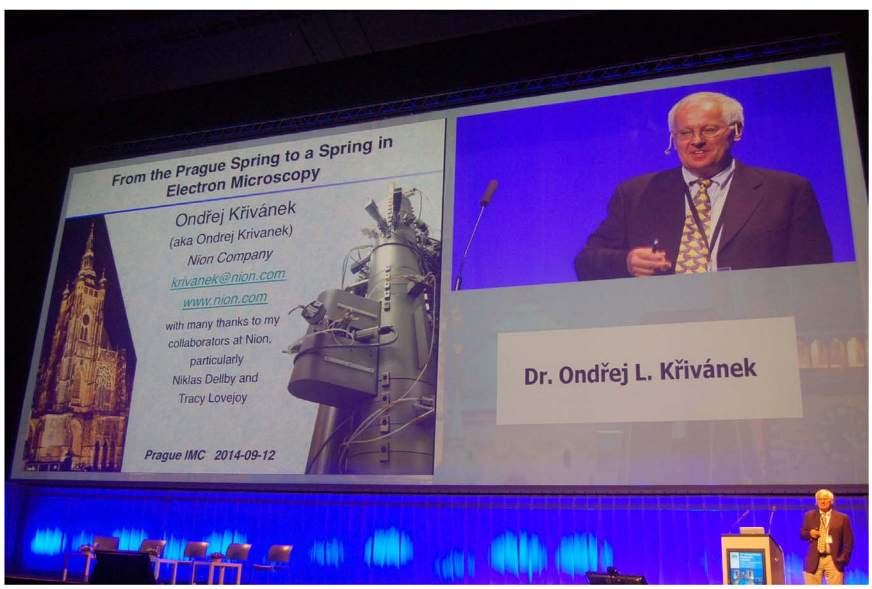

Fig. 9. Ondrej Krivanek at the bottom right of the picture begins his presentation in the final session of ICM 18 in Prague [9], after having been awarded the IFSM V.E. Cosslett medal.

scientific review. The field of spatially resolved EELS has tremendously progressed over the past four decades, as is schematically illustrated in figure 11 of reference [32]. In a spatial resolution, energy resolution coordinate system, it started from about (1 nm, 1 eV) in the mid-sixties and it has now reached a domain of typically (0.1 nm, 0.1 eV) or (1 nm, 0.01 eV) with huge potentialities in terms of elemental mapping and bond mapping in the first case or of plasmonics and phononics in the second. For sure, over this period, Ondrej Krivanek, who had made up his mind immediately following our first encounter and exchange, has beautifully paved the way in electron energy-loss spectroscopy and associated techniques. I can fully testify to it. And to end, I have selected the picture, shown in Fig. 9, which was recorded during the final presidential session at the ICM meeting in Prague, when he was awarded with the Vernon E. Cosslett medal of the IFSM (International Federation of Societies of Microscopy. With all my congratulations to Ondrej!

References

[1] M. Isaacson, D. Johnson, The microanalysis of light elements using transmitted energy loss electrons, Ultramicroscopy 1 (1975) 33–52.
[2] C. Colliex, V.E. Cosslett, R.D. Leapman, P. Trebbia, Contribution of electron energy loss spectroscopy to the development of analytical electron microscopy, Ultramicroscopy 1 (1976) 301–315.
[3] R.F. Egerton, TEM-EELS: a personal perspective, Ultramicroscopy 110 (2012) 24–32.
[4] A.V. Crewe, M. Isaacson, D. Johnson, Electron energy-loss spectra of the nucleic acid bases, Nature 231 (1971) 262–263.
[5] (a) M. Isaacson, Interaction of 25 keV electrons with the nucleic acid bases, adenine, thymine and uracil, Outer shell excitation, J. Chem. Phys. 56 (1972) 1803–1812;
(b) M. Isaacson, Interaction of 25 keV electrons with the nucleic acid bases, adenine, thymine and uracil. Inner shell excitation and inelastic scattering cross sections, J. Chem. Phys. 56 (1972) 1813–1818.
[6] C. Colliex, B. Jouffrey, Pertes d'énergie dans des couches minces de gaz solidifiés, J. Phys. 32 (1971) 461–466.
[7] C. Colliex, B. Jouffrey, Diffusion inélastique des électrons dans un solide par excitation de niveaux atomiques profonds. I - Spectres de pertes d'énergie, Philos. Mag. 25 (1972) 491–511.
[8] C.H. Chen, J. Silcox, R. Vincent, Electron-energy losses in silicon: bulk and surface plasmons and Čerenkov radiation, Phys. Rev. B 12 (1975) 64.

[9] O.L.Krivanek, From the Prague Spring to a spring in electron microscopy, *Proceeding 18thInternational Microscopy Congress Prague*, ⟨http://www.microscopy.cz/abstracts/6100.pdf⟩, 2014.
[10] O.L. Krivanek, P.R. Swann, An advanced electron energy loss spectrometer, *Proceedings Quant. Microanal. with High Spatial Res.* (Metals Society, London, 1981), pp. 136–140.
[11] C.C. Ahn, O.L. Krivanek, EELS Atlas - a reference guide of electron energy loss spectra covering all stable elements, ASU HREM Facility & Gatan Inc, Warrendale, PA, 1983.
[12] C. Jeanguillaume, O.L. Krivanek, C. Colliex, Optimum design and use of homogenous magnetic field spectrometers in EELS, in: Proceedings EMAG 1981, Inst. Phys. Conf. Ser. 61, 1981, pp. 189–192.
[13] C. Colliex, O.L. Krivanek, P. Trebbia, Electron energy loss spectroscopy: a review of recent progress, in: Proceedings EMAG 1981, Inst. Phys. Conf. Ser., 61, 1981, pp. 183–188.
[14] Electron-beam-induced spectroscopies with high spatial resolution, Selected papers from the NSF/CNRS workshop, Aussois, France 1988, Guest editors C.Colliex, M. Isaacson, Ultramicroscopy, vol. 28, 1989, pp. 1-375.
[15] A. Eades, Summary: one- and two-dimensional electron detectors, Ultramicroscopy 28 (1989) 209–210.
[16] O.L. Krivanek, Improved parallel-detection electron energy-loss spectrometer, Ultramicroscopy 28 (1989) 118–121.
[17] H. Shuman, Parallel recording of electron energy-loss spectra, Ultramicroscopy 6 (1981) 163–168.
[18] H. Shuman, P. Kruit, Quantitative data processing of parallel recorded electron-energy loss spectra with low signal to background, Rev. Sci. Inst. 56 (1985) 231–239.
[19] H. Shuman, A.P. Somlyo, Electron energy loss analysis of near-trace-element concentrations of calcium, Ultramicroscopy 21 (1987) 23–32.
[20] O.L. Krivanek, C.C. Ahn, R.B. Keeney, Parallel-detection electron spectrometer using quadrupole lenses, Ultramicroscopy 22 (1987) 103–116.
[21] D. Bouchet, et al., Analytical electron microscopy at the atomic level with parallel electron energy loss spectroscopy, Microsc. Microanal. Microstruct. 1 (1990) 443–445.
[22] O.L. Krivanek, C. Mory, M. Tencé, C. Colliex, EELS quantification near the single atom limit, Microsc. Microanal. Microstruct. 2 (1991) 257–267.
[23] R.D. Leapman, J.A. Hunt, Comparison of detection limits for EELS and EDXS, Microsc. Microanal. Microstruct. 2 (1991) 231–244.
[24] K. Suenaga, et al., Element-selective single atom imaging, Science 290 (2000) 2280–2282.
[25] C. Jeanguillaume, C. Colliex, Spectrum-image: the next step in EELS digital acquisition and processing, Ultramicroscopy 28 (1989) 252–257.
[26] J.A. Hunt, D.B. Williams, Electron energy-loss spectrum-imaging, Ultramicroscopy 38 (1991) 47–73.
[27] G. Balossier, et al., Parallel EELS elemental mapping in scanning transmission electron microscopy: use of the difference methods, Microsc. Microanal. Microstruct. 2 (1991) 531–546.
[28] C. Colliex, et al., Electron energy-loss mapping, Mikrochim. Acta 114/115 (1994) 71–87.
[29] J.L. Lavergne, J.M. Martin, M. Belin, Interactive electron energy-loss elemental mapping by the “Imaging-Spectrum” method, Microsc. Microanal. Microstruct. 3 (1992) 517–528.
[30] O.L. Krivanek, A.J. Gubbens, N. Dellby, C.E. Meyer, Design and first applications of a post-column imaging filter, Microsc. Microanal. Microstruct. 3 (1992) 187–199.
[31] Lake Tahoe workshop on electron energy loss spectroscopy 1990, Proceeding, Guest editor O.L. Krivanek, Microsc. Microanal. Microstruct., vol. 2, 1991, pp. 143–411.
[32] A. Gloter, et al., Atomically resoled mapping of EELS fine structures in pressMater. Sci. Semicond. Process. (2016). http://dx.doi.org/10.1016/mssp. 2016.07.006 in press.
[33] O.L. Krivanek, A.J. Gubbens, N. Dellby, Developments in EELS instrumentation for spectroscopy and imaging, Microsc. Microanal. Microstruct. 2 (1991) 315–332.
[34] O.L. Krivanek, et al., High-energy-resolution monochromator for aberration-corrected scanning transmission electron microscopy/ electron energy-loss spectroscopy, Philos. Trans. R. Soc. A 367 (2009) 3683–3698.
[35] O.L. Krivanek, T.C. Lovejoy, N. Dellby, R.W. Carpenter, Monochromated STEM with a 30 meV-wide, atom-sized electron probe, Microscopy 62 (2013) 3–21.
[36] O.L. Krivanek, et al., Vibrational spectroscopy in the electron microscope, Nature 514 (2014) 209–212.
[37] P. Rez, et al., Damage-free vibrational spectroscopy of biological materials in the electron microscope, Nat. Commun. (2016). http://dx.doi.org/10.1038/ncomms10945.
[38] M. Isaacson, C. Colliex, Summary and conclusions of the Aussois workshop, Ultramicroscopy 28 (1989) 363–368.