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Science in the making 2: From 1940 to the early 1980s / *La science en mouvement 2 : de 1940 aux premières années 1980*

The "father" of microanalysis: Raymond Castaing, creator of a generation of scientific instruments, still in worldwide operation

Le « père » de la microanalyse : Raymond Castaing, créateur d'une génération d'instruments scientifiques encore opérationnels dans le monde entier

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ABSTRACT

This manuscript emphasizes the leading role of Raymond Castaing in the conception, realization, and use of three major families of scientific instruments for local analysis of matter. Starting from his early studies with his research director, André Guinier, on the visualization of the GP zones in metal alloys, Raymond Castaing has introduced different stages of innovation for the identification of the elements present in the smallest volume of material. These were successively the X-ray electron probe, the secondary ion mass spectrometry with his student Georges Slodzian, the electron energy-loss filtering with his student Lucien Henry. Besides his Ph.D. dissertation, a reference text on any aspect of electron beam induced X-ray microanalysis, Raymond Castaing has continuously published, over a period of three decades, his research in the successive issues of the *Comptes rendus de l'Académie des sciences*

RÉSUMÉ

Ce manuscrit décrit le rôle pionnier et déterminant de Raymond Castaing dans la conception, la réalisation et l'utilisation de trois familles majeures d'instruments scientifiques destinés à l'analyse locale des matériaux. À partir de ses premières recherches avec son directeur de thèse André Guinier sur la visualisation directe des zones GP dans des alliages métalliques, Raymond Castaing a introduit plusieurs générations d'innovations dédiées à l'identification des éléments présents dans le plus petit volume de matière. Ce furent successivement la microsonde X, l'analyse par spectrométrie de masse des ions secondaires avec son élève Georges Slodzian et l'analyse par filtrage d'énergie des électrons transmis en microscopie électronique avec son élève Lucien Henry. Outre son manuscrit de thèse, véritable « bible » couvrant tous les aspects de l'analyse des rayons X émis sous incidence d'un faisceau d'électrons primaires, Raymond Castaing a publié de façon permanente, pendant

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trois décennies, ses recherches dans les volumes successifs des *Comptes rendus de l'Académie des sciences*.

Seeing the invisible has been a permanent quest for the human being and has stimulated a large number of efforts to create tools to push further our field of vision into the domain of the small and ultrasmall. It is possible to start with the first optical microscope, built in the late seventeenth century by Antoni von Leeuwenhoek in Holland, which allowed him to discover unicellular organisms. A major step forward has been, around 1930, the use of electron beams instead of photon beams, which has opened a breakthrough in spatial resolution as a consequence of the strong wavelength reduction of the associated waves. The first electron microscope, built by Knoll and Ruska in Berlin, generated a lot of technical developments which brought the accessible spatial resolution down to 10 nm in 1939. Together with the preparation of thin specimens, a first generation of images was produced, revealing the sub-micron structure of particles, metals, and ceramics.

At the same time (1937), in two notes published in the *Comptes rendus*, Guinier [1] and Jacquet [2] described some experimental progress that will generate some non-negligible impact into the research domains explored in the following years. Jacquet introduced a method relying on electrolytic reactions to produce a perfect polishing of the surfaces of thin metallic layers. As for Guinier, in the preparation of his thesis at the "École normale supérieure", University of Paris to be defended in 1939, he built a monochromatic X-ray illumination system providing diffraction patterns of much increased quality. With this system in hands, he could solve crystalline structures on samples made of large crystals. And in 1938, he described [3] a new type of diffraction pattern recorded on a series of aluminum–copper alloys, exhibiting unusual streaks that he interpreted as due to the coalescence of Cu clusters of typical sizes 150 Å in diameter and 3 to 4 Å in thickness. A following publication of these results by Guinier in Nature [4] provoked a comment in the same issue of the *Nature* journal by Preston [5] reporting similar results in support of their interpretation of a second phase in these age-hardened alloys. This was the birth of the Guinier–Preston (GP) zones to be further discovered in many alloys.

This subject reappeared after war when Guinier asked one young student to enrich these observations in the diffraction world with direct imaging in an electron microscope, the performance and domain of use of these instruments having also progressed during this period. This student, Raymond Castaing, had been hired at that time (1947) as an "ingénieur des petites études" at Onera ("Office national d'études et de recherches aéronautiques") to prepare a doctoral thesis under the supervision of André Guinier. Previously, Castaing had been admitted at the "École normale supérieure", Paris, in 1940, joined the French resistance during the war, and graduated in 1946 as an "agrégé" in physics, the highest grade for teaching physical sciences. During the year 1949, Castaing and Guinier published three notes in the *Comptes rendus* [6–8], reporting the technique used in electron microscopy (the observation of oxide replicas of the specimen's surface) and its application to the study of platelets created in aluminum–copper and aluminum–magnesium–silicon alloys hardened by heat treatments. If this printing technique has provided hints of the presence of platelets in epitaxy with the [100] lattice planes of the matrix, it has failed to directly image the first gathering of Cu atoms as suggested by X-ray diffraction techniques to be of very small size below the resolution of the technique. Five years later, after having improved the polishing technique (electrolysis followed by ion irradiation) [9], clean thin foils of alloys were obtained and examined in a transmission electron microscope. Castaing and Lenoir could then image with weak contrast Guinier–Preston zones in an Al–Cu_4% foil in its first stage of heating [10].

Beforehand, during the early years of his thesis preparation, another idea had emerged between Guinier and Castaing: would it be possible to push the technique beyond imaging these small objects, the zones of copper precipitation in the aluminum matrix, i.e. analyzing them. The basic idea was to direct onto a particular point on the specimen surface a finely focused electron beam, the electron probe, and to collect and analyze the wavelength of the emitted X-rays under the electron impact in order to determine the local chemical composition. Guinier had established himself at that time as an expert in X-ray diffraction. At ONERA, Castaing could use a CSF 3M electron microscope with electrostatic lenses resulting from the work of Grivet and then made commercially available. He first devoted most of his attention to the production of 30-kV electron beams focused into small probe sizes (about 1 µm in diameter) and carrying a maximum current (typically 10^{-8} A) in order to generate X-ray emission fluxes sufficiently intense to be measured. This search required efforts to understand, model, measure, and reduce the effects of the aberrations of the electron lenses, in particular those associated with astigmatism [11–13].

The first demonstration of the successful use of these fine electron probes for the elemental analysis of solid specimens was made public during international conferences of electron microscopy in Delft (1949) and Paris (1950) and published, co-authored by Castaing and Guinier in the associated proceedings [14,15]. This latter contribution describes the design of the instrument realized by Castaing with his CSF microscope (see Fig. 1). A new objective lens made of two reducing electrostatic lenses, which, together with the astigmatism corrector, delivers a current varying from 10^{-8} A to 10^{-7} A in a spot of 0.5 to 2 µm. The X rays leave the column through a thin Al window and are analyzed with a home-built curved quartz spectrometer and a Geiger counter as the detector. Typically, on a Cu sample, an intensity of the $K\alpha_1$ line greater than 100 counts per second is recorded for a 1-µm probe of 30-kV electrons. Fig. 2 shows a view of the whole microscope equipped with this wavelength-dispersive spectrometer.

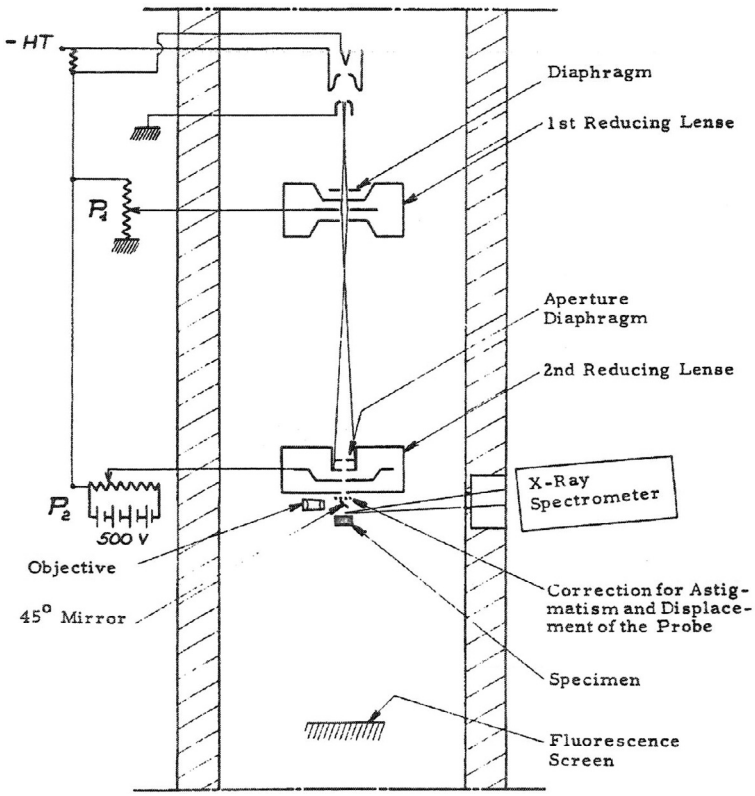


Fig. 1. Scheme of the first electron microprobe realized by transformation of a CSF electrostatic microscope (from R. Castaing's Ph.D. manuscript, 1951).

Surprisingly, during the next couple of years, we cannot find in the open literature, including the *Comptes rendus*, any text published by Castaing relatively to this new instrument as an analyzing tool and its performance or field of use. By the way, there is a short note in which Castaing mentions that it enables one to record diffraction patterns of the emitted X-rays, the Kossel lines, to identify crystalline structures [16]. As a matter of fact, he concentrates all his efforts into writing down his doctorate manuscript. The oral presentation took place at the Paris University in June 1951 and the written version, entitled "Application des sondes électroniques à une méthode d'analyse ponctuelle, chimique et cristallographique", was published by ONERA in 1952 [17] (Fig. 3).

This is actually a very rich text. Beyond a detailed description of the instrument together with the required technical innovations to obtain its best performance in terms of resolution and signal, it contains the basic theory of the physical processes involved in the X-ray emission processes. How far can we relate the intensity of an emitted X-ray line to the concentration of the corresponding element in the analyzed volume: this is the basis of quantitative analysis. Castaing's thesis introduces and indicates how to calculate the main terms to be considered for a satisfactory quantitative analysis: (i) the distribution in depth of the characteristic X-ray emission $\phi(\rho z)$, and the adverse correction factors to be applied to the intensity of the X-ray line, i.e. (ii) the absorption of the emitted X-rays in the analyzed material itself (absorption), or (iii) their excitation by another characteristic or background radiation (fluorescence). This will be the basis of the largely used ZAF method developed fifteen years later by Philibert and Tixier [18]. Meanwhile, it is interesting to point out Castaing's special interest for the study of the distribution in depth of the X-ray emission from the surface of a material, which he investigated experimentally with Descamps [19].

At that point, it is interesting to mention that the content of the thesis of Castaing, written in French as all his publications until that date, was recognized sufficiently rich to deserve a translation in English, made by Pol Duwez and David Wittry at Caltech and published as a technical report under the support of the US Department of Army in 1955 [20]!!! The interest of the US community for the work of Castaing may have grown after a meeting at the National Bureau of Standards dedicated to Electron Physics, which took place in November 1951. But the Proceedings came out only in 1954. They contain two texts from Castaing written in English: one is dedicated to the principle and corrections in microanalysis by means of an electron probe and can be read as a long summary of his thesis. The second describes first applications in the metallurgical domain including the use of the selective reflection of the emitted X-rays on well-oriented crystal planes for crystallographic identification and orientation of the probed volume of matter [21]. In the discussion following the second paper, it is interesting to read questions by famous scientists at that time, Marton and Gabor, and they deal with radiation damage and contamination!!!

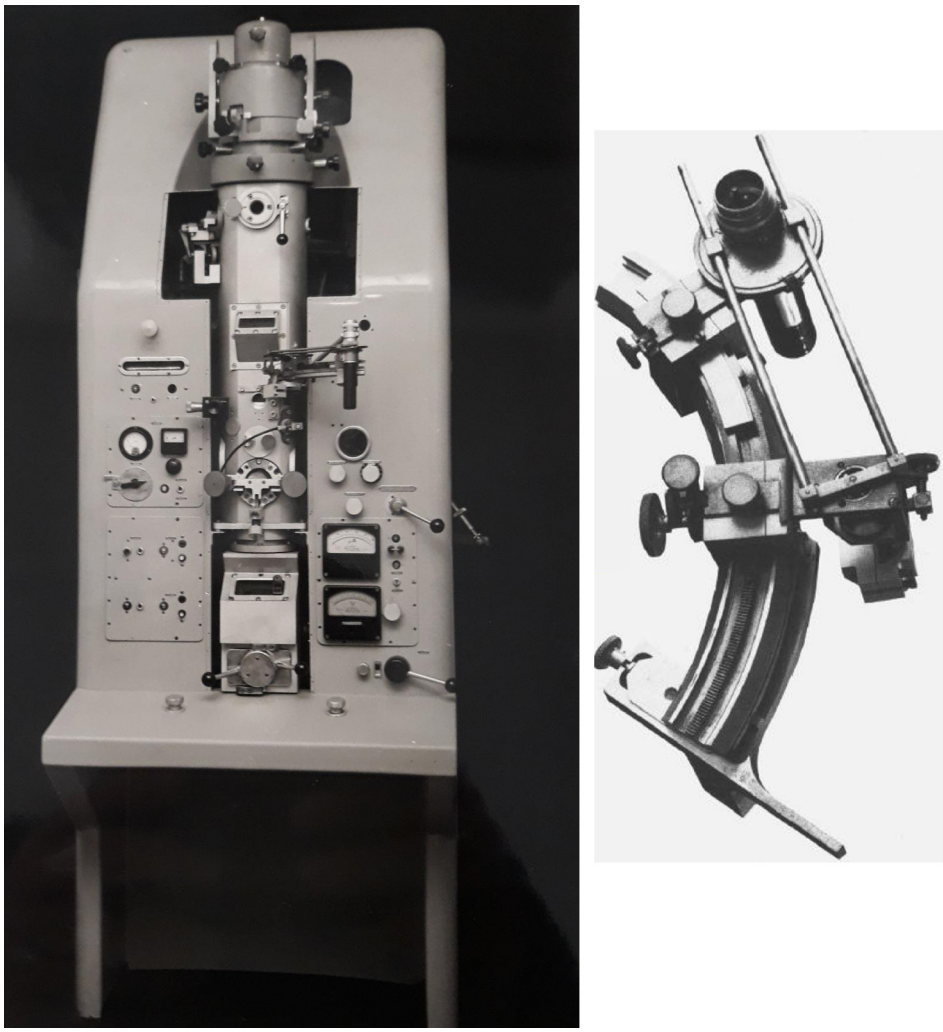
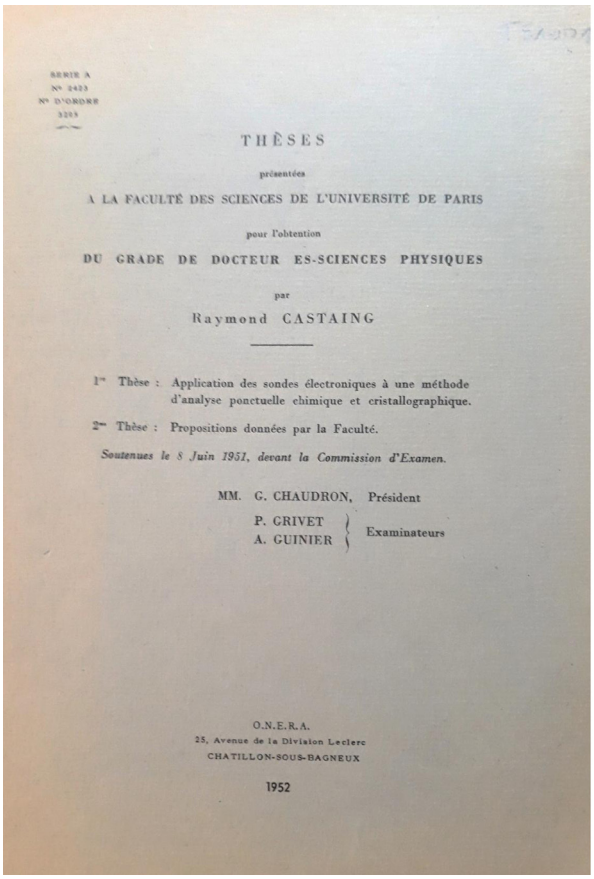


Fig. 2. Global view of the instrument schematized in Fig. 1 and detail of the spectrometer (from R. Castaing's thesis, 1951).

The role of Guinier becomes again important during the following period. He convinces IRSID (the French Institute of Research in Siderurgy) to support the design and building of a new prototype to further explore applications in metallurgy, using such arguments as "inclusions as small as a few microns can be analyzed". The first machine of this new generation was built at ONERA and delivered in 1955 to IRSID, where it became operated by Philibert. But a similar one was installed at ONERA and there operated by Castaing himself (Fig. 4).

This machine is noticeably different from the first prototype: a magnetic lens is used to focus the beam on the specimen; it incorporates an optical microscope for direct localization of the beam on the specimen surface and two X-ray spectrometers are placed under vacuum in front of the specimen, therefore improving the collection of X-rays. This is really the "first" microanalyzer. It will be made commercially available as the MS58 instrument in 1958 by the French company CAMECA and delivered in various places in France (CEA, CNET, BRGM) as well as in the USA. Castaing gave a first description of the present state of the realization of this new instrument during the International Electron Microscopy Conference in London in 1954 [22], and published together with Descamps an extended report on the different parameters involved in the emission process that can govern the accuracy of a quantitative measurement [23]. Finally, one can find a full review text on Electron Probe Microanalysis in English in 1960 [24].

During this period, many users from quite different research fields demonstrated the power of this instrument in domains far from the originally and most explored one in metallurgy [25]: for instance, in geology [26] and in medicine [27], which then became great customers of microanalytical characterizations. In the following years, CAMECA developed successive generations of X-ray microanalyzers, the most famous one being the Camébax instruments. One can read today on the CAMECA website the presentation of their most recent X-ray microanalyzer: "Since pioneering Electron Probe MicroAnalysis in the 1950s, CAMECA has released several generations of microprobes, all with a proven valuable track record for analytical



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THÈSES

présentées

A LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ DE PARIS

pour l'obtention

DU GRADE DE DOCTEUR ES-SCIENCES PHYSIQUES

par

Raymond CASTAING

1re Thèse : Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et cristallographique.

2me Thèse : Propositions données par la Faculté.

Soutenues le 8 Juin 1951, devant la Commission d'Examen.

MM. G. CHAUDRON, Président
P. GRIVET, A. GUINIER } Examinateurs

O.N.E.R.A.
25, Avenue de la Division Leclerc
CHATILLON-SOUS-BAGNEUX

1952

Fig. 3. Cover of Raymond Castaing's Ph.D. manuscript, and the young laureate in 1951.

performance and reliability. The new SXFive-TACTIS builds on this legacy to deliver enhanced imaging and quantitative analysis in a user-friendly environment."

Back to the fifties, the personal situation of Castaing changed rapidly as he entered the academic career as a young "maître de conferences" at the University of Toulouse in 1952, quickly followed by a professor position at the University of Paris (1956). He then moved in 1959 to the newly created "faculté des sciences d'Orsay" where, together with Friedel and Guinier, he founded the "Laboratoire de physique des solides" (LPS). This was the starting point of a new period of intensive research and innovation in the domain of... microanalysis!!!

Castaing was then following his quest of the design of an instrument delivering best compositional maps. He was not that fond of the idea of scanning a probe on the specimen, although this was the solution used in the X-ray microprobe. He was much more enthusiastic for particle optics systems delivering filtered images. In the LPS at Orsay, with two students, Slodzian, who had followed him from Toulouse, and Henry, he investigated and created two new research tools delivering chemical maps: (i) secondary-ion microscopy and spectroscopy (SIMS) and (ii) electron energy-loss imaging and spectroscopy (EELS). We can find the first reports on these two approaches in two notes in the *Comptes rendus* published in 1962 [28,29].

The secondary-ion microscope uses analytical signals carried by the secondary ions produced under the sputtering of the sample surface by primary ions, as suggested in a first demonstration of the potential of such a method for mapping the spatial distribution of the elements constituting the specimen [30]. These secondary ions are analyzed by a mass spectrometer that generates images of the elemental composition, but also of the isotope distribution. This instrument, the principle of which is shown in Fig. 5a, has required the development of the first imaging mass spectrometer relying on the focusing properties of the fringing field of a magnetic sector and a novel ion-to-electron image converter to obtain adequate images. A more complete description of this prototype and its first images was published at the same time in the *Journal de microscopie* [31], the publication of the French Society of Electron Microscopy (SFME), the first President and Founder of which was, by the way, Raymond Castaing. These images demonstrated the theoretical resolution limit, around 0.5 µm, imposed by aberrations arising from the angle and energy spread of the sputtered ions. The Slodzian's machine was then realized commercially by CAMECA as the SMI 300 ion microscope, introduced on the public market in 1968. Several generations of instruments have followed, bringing CAMECA to the leadership on the world market for this type of analyzer recognized as the most sensitive elemental and isotopic surface analysis [32]. With the NanoSIMS using a nanoprobe design realized at

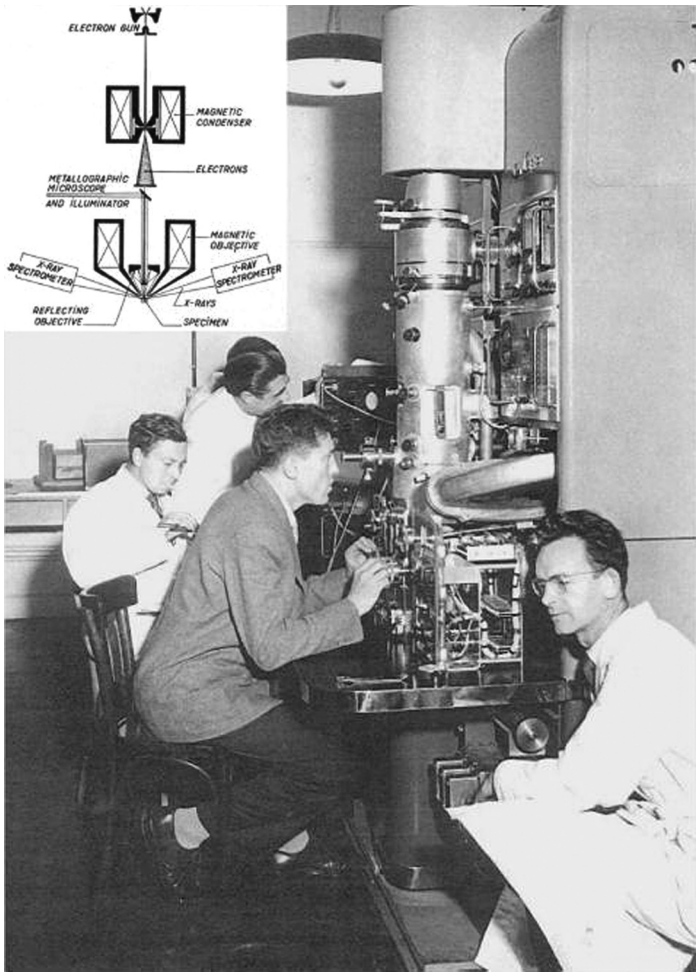

Fig. 4. Raymond Castaing operating the microprobe of the second generation developed at ONERA in the mid-fifties.

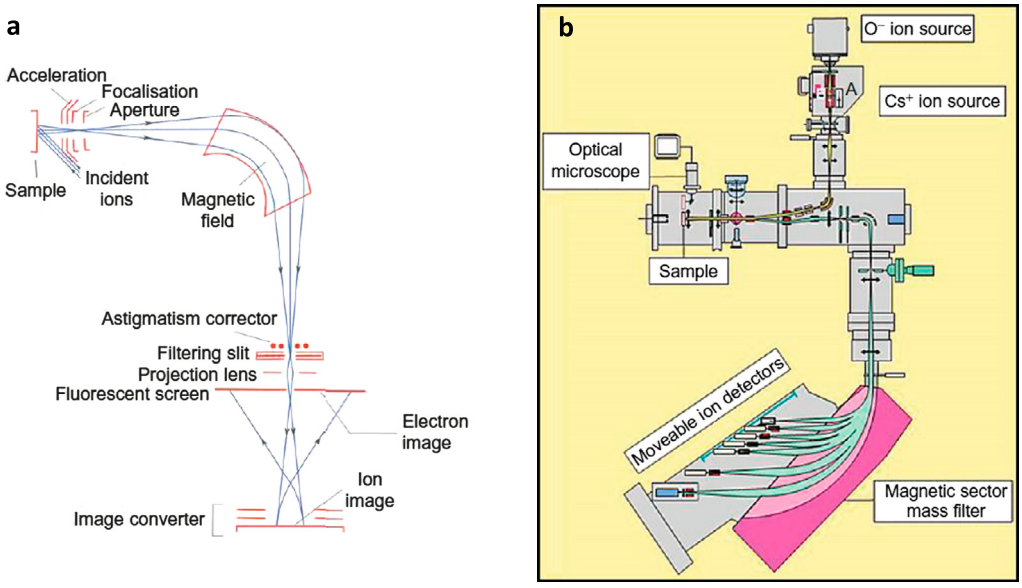

Fig. 5. (a) Diagram of the first secondary ion-microanalyzer built in 1962 (from Castaing and Slodzian [28]); (b) prototype of the NanoSIMS developed by CAMECA in the mid-nineties, equipped with a mass spectrometer of the Mattauch and Herzog types.

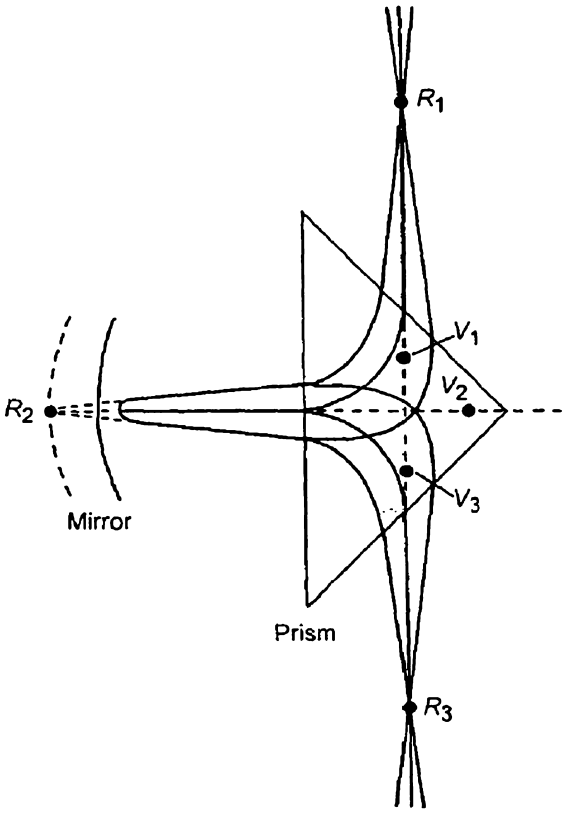

Fig. 6. Scheme of principle of the energy filtering device, known as the Castaing and Henry filter, developed for electron energy-loss analysis and filtering on the column of a conventional transmission electron microscope (from [29]).

ONERA under supervision by Slodzian, it provides an extremely high sensitivity for all elements from hydrogen to uranium and above (down to the ppb level for many elements), together with a high lateral resolution imaging down to 40 nm. This is by definition a destructive technique as it relies on the sputtering of the surface layers, which can become a very powerful tool for in-depth analysis of trace elements with a depth resolution ranging from the sub-nanometer scale to tens of nanometers. Fig. 5 compares the principles of the instruments built by Slodzian for his thesis in 1963 and for NanoSIMS in 1997.

The second major project led by Castaing in the early sixties together with his student Henry was to insert an electron energy spectrometer within the column of a transmission electron microscope. One could thus measure the energy loss suffered by the primary electrons across the specimen and use those electrons having lost a given energy and therefore contributing to a specific excitation, to realize energy-filtered images. The electron-optical system designed and built for this purpose is a dispersive system made of the association of a magnetic sector with an electrostatic mirror, as shown in Fig. 6. Such a design exhibits, for a satisfactory excitation of the mirror, two couples of stigmatic points, one real, R_1 and R_3, and one virtual, V_1 and V_3. An energy loss spectrum is formed at the level of R_3 and a filtered image is formed at the level of V_3 when a slit is introduced in R_3 to select an energy window corresponding to the desired energy loss ΔE with a given energy width δE.

In a following note [33], Castaing et al. demonstrated that this technique could constitute a new method for qualitative microanalysis at high resolution, as illustrated in Fig. 7. This is demonstrated in the thesis work by Lucien Henry (1964) and Ali El Hili (1967). Fig. 7 shows how energy-loss spectra (a) can be used to produce chemical maps. The specimen is a partially oxidized thin foil of aluminum with two characteristic spectra showing plasmon peaks at 15 eV in Al and at 6.5 and 21 eV in Al_2O_3. The left-hand-side image in (b) corresponds to a zero-loss image; it reveals the presence of a continuous layer; the central one filtered with a 1.5 eV slit around 6.5 eV displays, with a strong white contrast, the presence of alumina on given areas, while the right-hand-side one, filtered with a width of 1.5 eV around the 15-eV line, confirms the presence of an aluminum foil between the oxide areas. In the following years, Castaing and his coworkers deepened the understanding of the origin of the diffraction contrast carried by inelastically scattered electrons [34].

This was the starting point of a long story accompanying the growing role of electron energy loss spectroscopy which became a very popular acronym – EELS – in the mid-70s as an undisputable micro- and nano-analytical tool. Colliex and Jouffrey in Raymond Castaing's lab in Orsay installed an energy-loss filter and spectrometer of Castaing and Henry type on a modern TEM at that time, an Hitachi HU11B, and then demonstrated the role of the EELS signals associated with specific

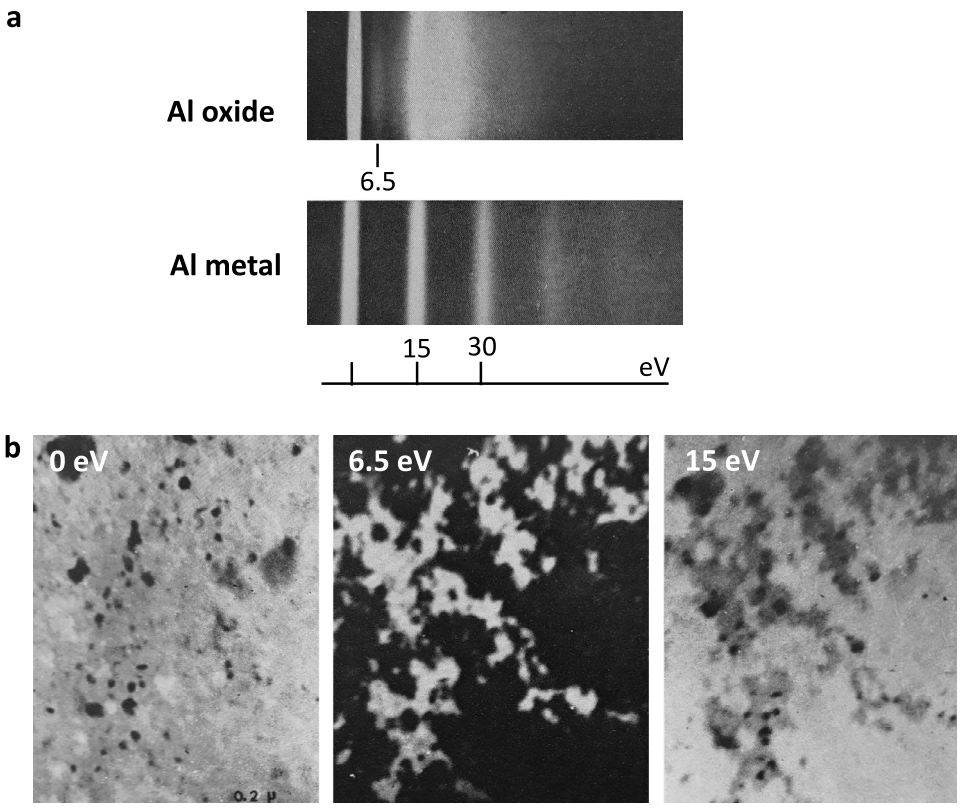

Fig. 7. Examples of electron energy-loss spectra and associated energy filtered images recorded on a partially oxidized aluminum thin foil (from Lucien Henry thesis work, 1964).

Fig. 8. A well-known portrait of Raymond Castaing accompanied by a view of the personal sword he received as a testimony of his membership at the French Academy of Sciences.

core-level excitations as true signatures of the presence of given elements under the impact of the primary electrons in the microscope. This research was also published in the *Comptes rendus* in 1970 [35,36]. Many years later, using an alternative approach, i.e. recording a whole electron energy-loss spectrum for all the positions of a sub-nanometer electron probe, we succeeded in identifying individual single atoms of rare-earth elements [37]. And today, all electron microscopes of the latest generations are equipped with an energy-loss analyzer and filter, the Gatan company being the major supplier of such devices on the world.

Being the creator of the three major microanalytical tools, the X-ray Microprobe, the Secondary Ion Mass Spectrometer, and the Electron Energy-Loss spectrometer, Raymond Castaing is undoubtedly the "father" of microanalysis. His influence has spread over many diversified fields of research from metallurgy to biomedicine. One can find in the recent literature reviews of the latest developments of these techniques [38–41] and can come across examples of applications in domains as different as dentistry [42], earth mantle [43], atmospheric particles [44], or the detailed atomic and electronic structures at oxide interfaces, which are responsible of some of the most intriguing behaviors [45] now observed in condensed-matter physics (colossal magnetoresistance, colossal ionic conductivity, ferroelectricity…). In recognition of these superb realizations and achievements, his role has fairly been recognized by many awards and in particular the gold medal of CNRS in 1975 and his election at the French Academy of Sciences in 1977, a fully deserved honor celebrated with the attribution of his personal academician sword (Fig. 8).

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