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PHOTOEMISSION AND FREE ELECTRON LASER SPECTROMICROSCOPY: PHOTOEMISSION AT HIGH LATERAL RESOLUTION

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Abstract

The move of photoemission analysis from the macroscopic to the microscopic domain has been accelerated by the advent of new ultrabright synchrotron sources of soft-X-rays. This makes an overview of photoemission spectromicroscopy, photoemission at high lateral resolution, quite timely. The overview begins with the basic concepts and problems, both technical and of data-taking strategy. Then, it presents a small number of examples of results in physics and biology, such as local chemical fluctuations in superconductors, semiconductor interfaces and the microchemistry of biological systems. The presentation includes the first experimental results from two new ultrabright synchrotron facilities: ELETTRA (in Italy) and SRRC (in Taiwan).

Key Words: Photoemission, electron microscopy, X-ray absorption, synchrotron radiation, spectromicroscopy, surfaces, interfaces, neurobiology, semiconductors, superconductors.

Introduction: What Is Photoelectron Spectromicroscopy?

Electron microscopy is usually based on the interaction between a primary electron beam and the system under investigation. There are different electron microscopy techniques, but all of them primarily deliver morphological information. However, some techniques can also deliver information on the local electronic and chemical structure, for example by performing electron energy loss spectroscopy on a microscopic scale.

Energy loss spectroscopy is only one of the many different spectroscopies based on electrons. For many years, the leading technique in electron spectroscopy has not been energy loss, but photoelectron spectroscopy. The superiority of photoelectron spectroscopy over other techniques is based on three points:

- The primary beam particles, photons, are gentler probes than, for example, ions or electrons; given a certain amount of extracted information, photons are less likely than other particles to cause damage and substantially modify the specimen under investigation.
- The photoelectric effect depends on a large number of variables that can be tuned, scanned or otherwise controlled [19]. This enhances the quality and quantity of information that can be extracted on the electronic and chemical structure.
- Photoemission spectroscopy has reached rather impressive levels of angular and energy resolution [19], and this again enhances, qualitatively and quantitatively, the information that is potentially available.

Why, then, do not we see electron microscopes based on the photoelectric effect in which photons are used as primary probes? The answer, in the first place, is that the signal level in a typical photoemission experiment is too low to allow lateral resolution better than 0.5 mm. On the other hand, this is no longer a general limitation; since the late 1980's, we have seen a rapid development of new experimental techniques, which are indeed able to couple photoelectron spectroscopy and high lateral resolution [1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 20, 22, 23, 25, 26, 27, 28, 29].

Before commenting in detail about the practical implementation of these techniques, it is important to discuss their comparative merits with respect to other experimental tools. I believe that the most illuminating comparison is with the techniques based on the scanning tunnel microscope (STM).

The STM has undeniably a superior performance levels as far as lateral resolution is concerned. In certain cases, it can reach the atomic ($\approx$ 1 Å) level. On the other hand, the practitioners of STM techniques are well aware of one limitation: one can "see" atoms, but one does not really know "what" atoms they are. This is a consequence of the limited spectroscopic capabilities of the STM, which in turn are a consequence of the very nature of the tunneling effect on which the STM is based.

On the other hand, conventional photoemission is a powerfool tool to determine the chemical properties of a system. The mere presence of photoelectrons excited from a given core level is clear evidence for the presence of the element to which the core level belongs. It is quite easy to distinguish one element from the others, because the typical distance in energy of the corresponding core levels is of the order of several electron-volts, and the typical energy resolution in conventional photoemission easily reaches the 100 meV level.

Analyzing different elements is not difficult either, since conventional photoemission can easily span an energy range of the order of 100-1,000 eV or more, which contains easy-to-investigate core levels of most elements. Thus, energy resolution and energy domain are the key factors in the excellent chemical analytical capabilities of conventional photoemission.

On the other hand, the performances of conventional photoemission instruments are extremely limited as far as lateral resolution is concerned. Very far from imaging individual atoms like the STM, a typical photoemission experiment is confined to the domain of millimeters or fractions of millimeters.

We can realize, therefore, that there exists a complementarity between the "microscopy" performances and the "spectroscopy" performances. With the advent of techniques that combine spectroscopy and microscopy, it becomes necessary to assess the overall performances by taking both of these aspects into account.

A few years ago, I had proposed a combined merit figure to perform such an assessment, the so-called spectromicroscopy Q-parameter [20], defined as:

$$Q = \Delta E \; P \; (\delta L)^{-1}, \qquad (1)$$

where ΔE is the energy domain over which spectroscopy is performed, $P = E/\delta E$ is the energy resolving power (δE is the absolute energy resolution), and δL is the lateral resolution.

In the interplay between "microscopy" and "spectroscopy", the STM is the limit case for the latter, with excellent lateral resolution that brings the overall Q-parameter to an impressive level, typically $Q \approx 10^3$-10^4 eV/Å, limit value $Q \approx 10^5$ eV/Å. Close to the opposite limit, there is ordinary photoemission, with excellent spectroscopic capabilities but very limited lateral resolution, which brings the Q-parameter to $\approx 10^{-1}$ eV/Å.

The primary objective of the spectromicroscopy techniques discussed in this review is to improve the lateral resolution of photoemission. At present, the best overall performance is delivered by the scanning photoelectron spectromicroscope MAXIMUM [25] at the Wisconsin Synchrotron Radiation Center (planned to be transferred to the Berkeley Advanced Light Source in the near future). The Q-parameter of MAXIMUM reaches the 10^2 eV/Å level.

In the near future, with the use of the new ultrabright soft-X-ray sources such as ELETTRA (in Trieste, Italy) and the Advanced Light Source (ALS, Berkeley, CA) photoemission spectromicroscopy should reach Q-values of $\approx 10^3$ eV/Å. The probable limit would correspond to the combination of ultrahigh energy resolution ($P = 10^4$), lateral resolution in the 100 Å range, and spectral domain of the order of 103 eV, corresponding to $Q \approx 10^5$ eV/Å, quite comparable to the STM and also to other techniques like electron energy loss spectroscopy (EELS) imaging.

The STM and photoelectron spectromicroscopy, however, reach this overall performance level in complementary ways: the STM emphasizes lateral resolution whereas photoemission spectromicroscopy trades lateral resolution in exchange for superior spectroscopic capabilities. And, such capabilities are superior indeed (for a complete discussion of modern photoemission techniques, see, Margaritondo [19]). In essence, the spectroscopic information goes well beyond the mere presence of given elements, and concerns the chemical status of such elements, their participation to chemical bonds and to the corresponding electronic structure, screening and other collective phenomena, etc.

The complementarity of different spectroscopy and microscopic techniques has one important implication: one cannot use only one technique for all applications. Until the arrival (if feasible) of the "ultimate" spectromicroscopy technique, capable of delivering spectroscopic advanced information like photoemission on an atomic scale, we must use whatever technique is best for each task. The reader, therefore, is warned not to believe exaggerated claims by partisans of specific approaches: at the present time, no leading technique exists, but rather a mix of different approaches with complementary capabilities.

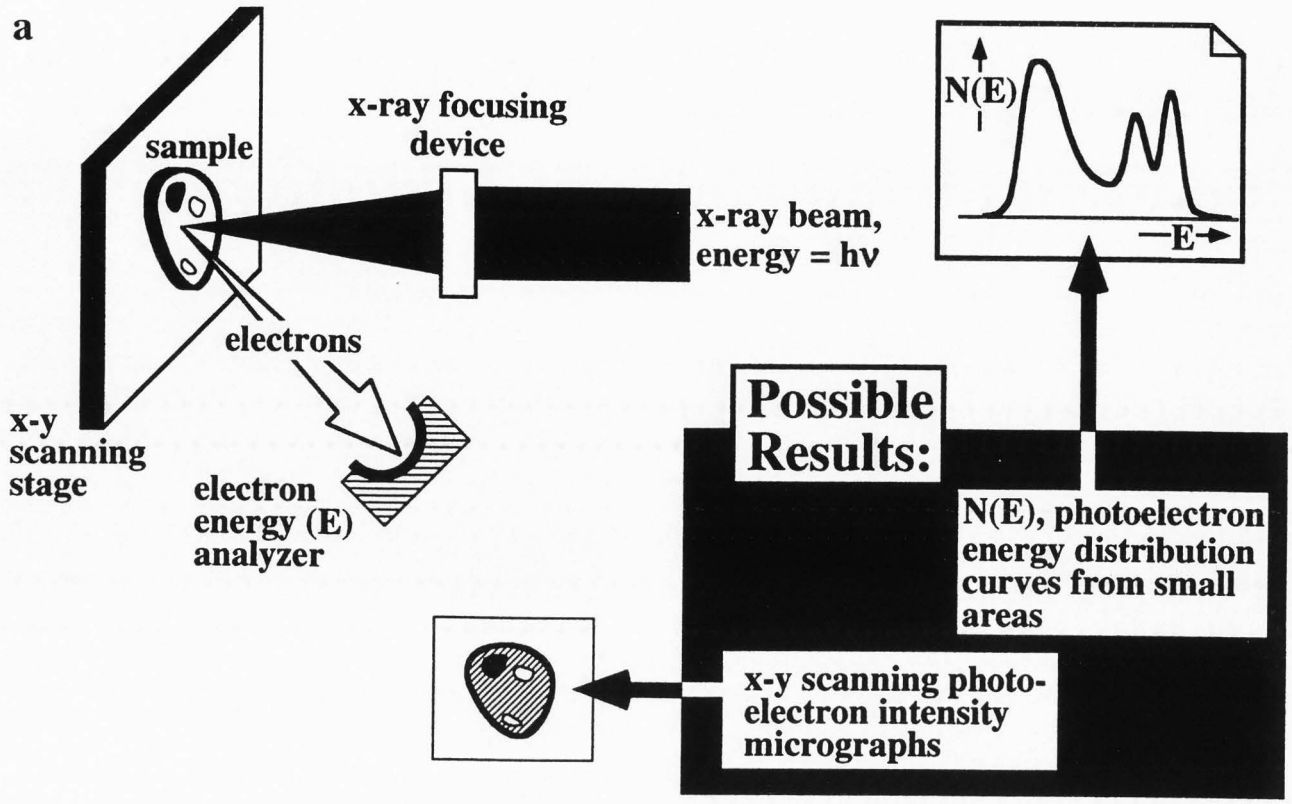
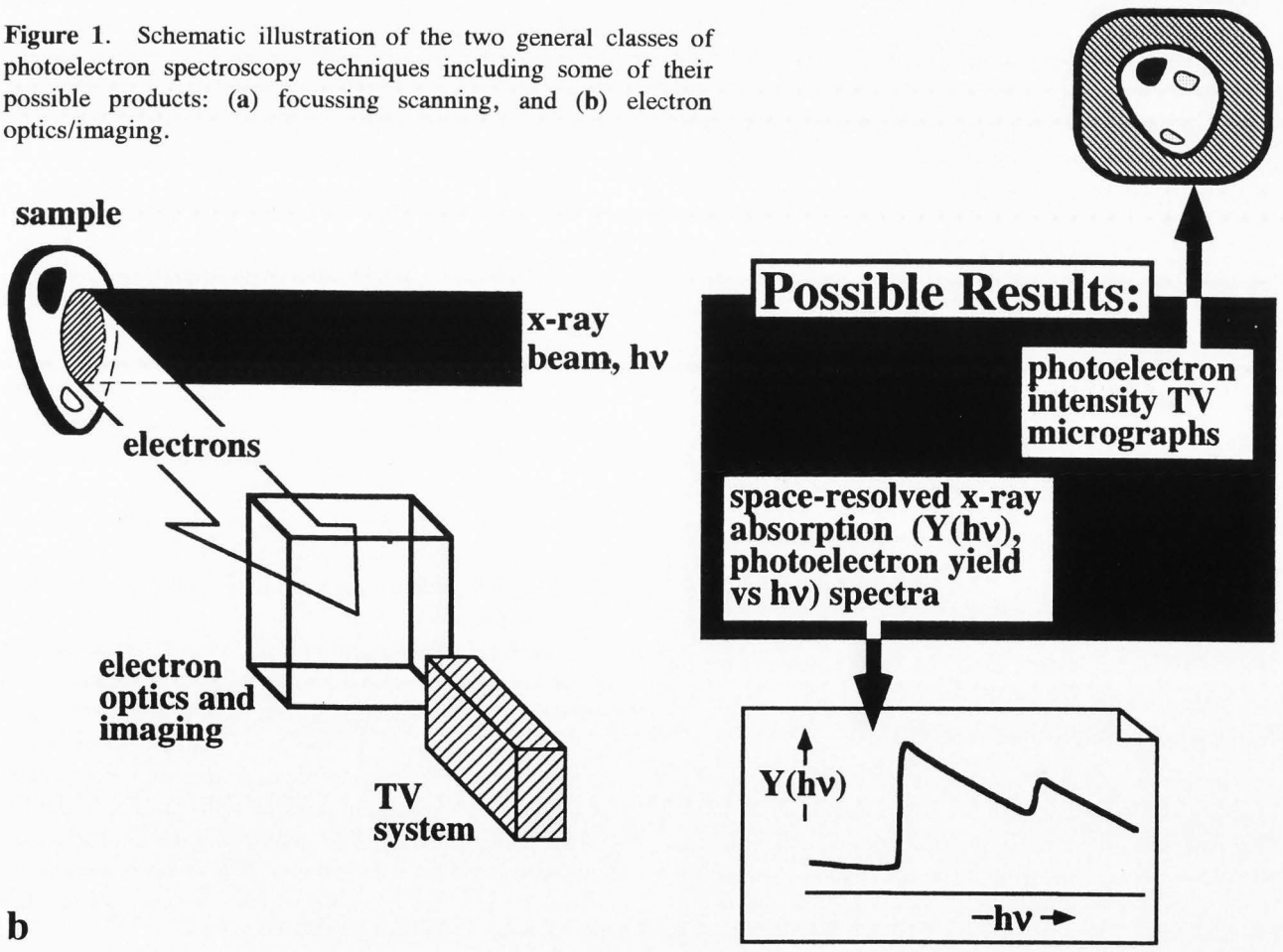


Figure 1. Schematic illustration of the two general classes of photoelectron spectroscopy techniques including some of their possible products: (**a**) focussing scanning, and (**b**) electron optics/imaging.



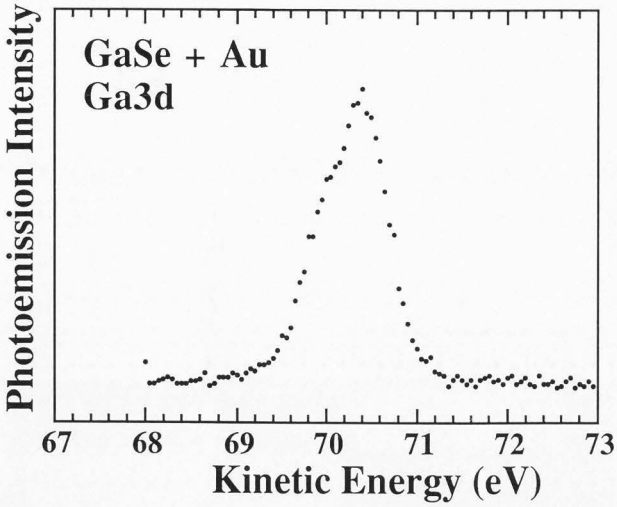


Figure 2. A typical photoelectron spectrum (taken on a GaSe surface covered with Au [10]). The mere presence of a peak, caused by photoelectrons excited from the Ga3d core level of GaSe, proves the presence of the corresponding element Ga in the specimen; additional analysis can deliver more sophisticated information, for example, on the chemical status of the element.

Before discussing the details of photoemission spectromicroscopy techniques and specific example from our own work, it is important to emphasize that this is no longer merely an area under development. Solid research programs have been active for several years, notably at Brookhaven, Wisconsin, Stanford, HASYLAB, Berkeley, and more recently at Taiwan [1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 20, 22, 23, 25, 26, 27, 28, 29]. We cannot provide here an overview of all of these programs; but we emphasize that our results are within a vigorous worldwide effort to which many other institutions participate.

Practical Approaches to Photoelectron Spectromicroscopy

The practical approaches to photoemission spectromicroscopy basically fall in two main categories: the focusing-scanning techniques [16, 17, 25] and the techniques based on electron optics and imaging [27, 28, 29]. The principles of these two categories are schematically summarized in Figure 1.

Focusing-scanning techniques

In this first case, the lateral resolution is reached by focusing an X-ray beam into a small spot [16, 17, 25]. This makes it immediately possible to take conventional photoemission spectra from the small area corresponding to the spot. A "conventional" photoemission spectrum is a plot of the distribution in energy of the collected

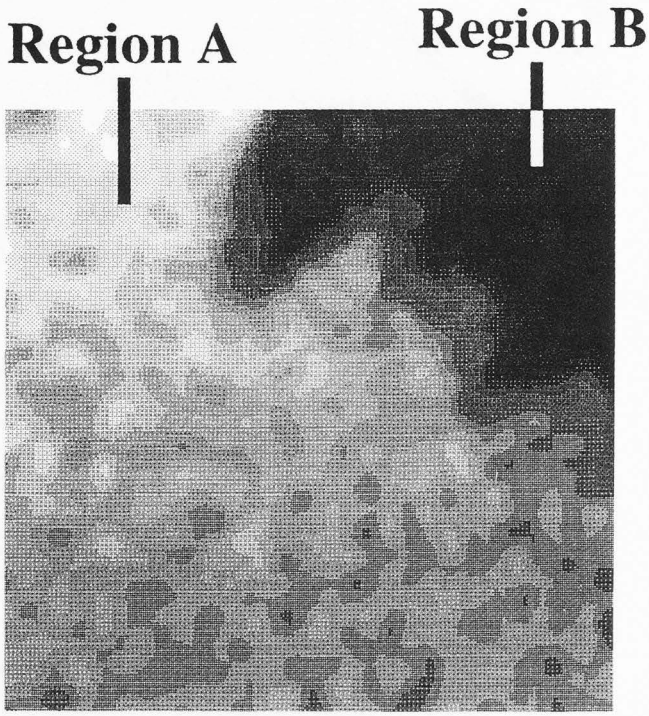


Figure 3. Scanning photoelectron micrograph of Au-covered GaSe [10], obtained by monitoring the intensity of photoelectrons excited from an Au state while scanning the sample position with respect to the focused photon beam. The Au overlayer thickness is different in regions A and B. Photo height = 80 μm.

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photoelectrons, whose emission is caused by an X-ray beam of fixed photon energy, $h\nu$ [19].

Suppose that the spectral range includes photoelectrons that were excited from a given core level of a given element (as seen, for example, in Figure 2); after measuring the energy position of the corresponding spectral peak, one can retrieve the initial core-level energy by simply subtracting $h\nu$. In this way, one gains information on the presence of the element and also on its chemical status. Similarly, by analyzing the energy distribution of photoelectrons originating from valence states, one can obtain sophisticated information on the chemical bonding processes and, in general, on the electronic structure.

Suppose now that, after detecting the presence of a given element in a certain area and after determining its chemical status, we want to see what is the distribution of the same element in the same status over a larger sample area. This is possible by acting on the x-y stage and scanning the sample position with respect to the focused photon beam, while monitoring the photoelectron intensity at the relevant energy. The result is a scanning photoelectron micrograph which contains all of the desired chemical information.

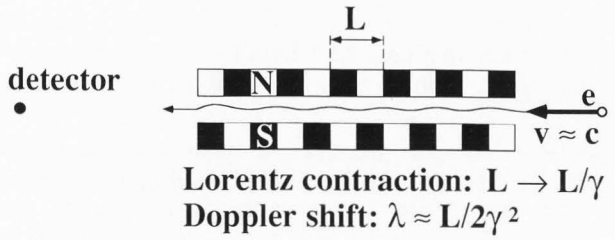

Figure 4. The basic operating principles of an undulator [21], for the emission of high-brightness synchrotron radiation.

One example a of scanning micrograph is shown in Figure 3: we see the spatial distribution of a metal overlayer over a GaSe substrate [10]. From the intensity changes, one can reveal differences in the thickness of the very thin gold overlayer.

The focusing-scanning approach is conceptually very simple. Its practical implementation, however, encounters two formidable practical problems: low signal level and difficulty in focusing X-rays.

The classic remedy to the first problem is to increase the intensity of the focused X-ray beam. This can be done by increasing the brightness of the photon source, which qualitatively corresponds to the flux divided by the source size and by the emitted beam's angular divergence. In the laboratory, this can be accomplished using high-flux rotating anodes. Truly superior sources, however, can only be found at synchrotron radiation laboratories: the so-called undulators [19, 21].

The operating principle of an undulator is illustrated in Figure 4 [21]: an electron that circulates at relativistic speed in a storage ring is forced to "undulate" around its trajectory, which would otherwise be a straight line, by a periodic array of magnets. Suppose that the array's period is L: the moving electron "sees" the magnet array as an electromagnetic wave, with wavelength equal to L/γ. The γ-factor is caused by the relativistic Lorentz contraction, and is given by:

$$\gamma = K/m_0c^2, \qquad (2)$$

the electron's (relativistic) energy K in units of m_0c^2, the electron's rest energy.

The interaction between the electron and the undulator's "wave" causes the emission of electromagnetic waves, whose wavelength is also L/γ in the electron's reference frame. In the laboratory frame, this wavelength is Doppler shifted, becoming in the first approximation:

$$\lambda \approx L/2\gamma^2 \qquad (3)$$

A more accurate treatment [21] actually predicts a dependence of the Doppler shift on the X-ray emission

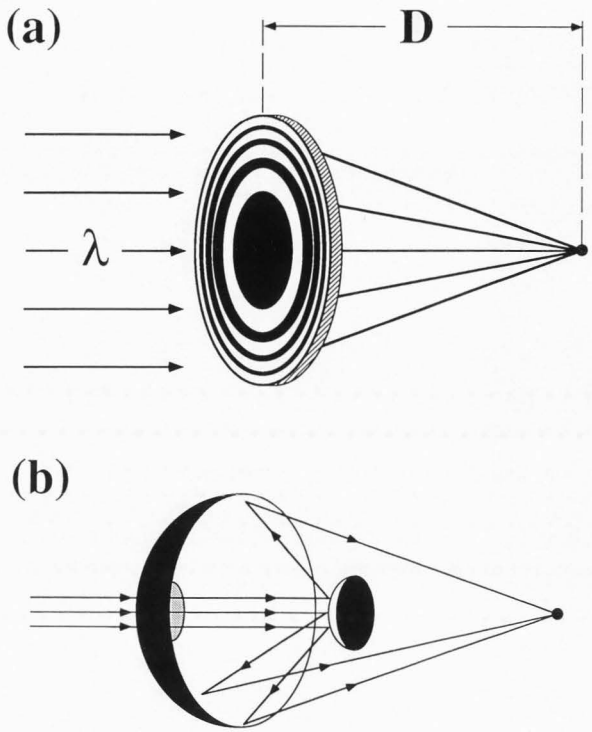

Figure 5. Schematic diagrams of focusing devices for soft-X-rays: (**a**) the transmission Fresnel zone plate [16, 17]; (**b**) the Schwarzschild objective [25].

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direction and on the strength of the magnetic field: this can be exploited to tune the emitted wavelength by changing B.

Note that the $2\gamma^2$ factor makes it possible to transform the undulator's period L (typically, a few centimeters) into a much shorter wavelength in the soft-X-ray range. Furthermore, the undulator produces an X-ray beam of extremely high brightness, basically for two reasons [21]. First, the emission is concentrated in a narrow wavelength bandwidth, around the aforementioned value $\lambda \approx L/2\gamma^2$. This is due to the fact that, for wavelength filtering, the undulator practically works as a diffraction grating. Second, the undulator's emission is concentrated in a very small solid angle. This angular collimation is a well-known relativistic effect, present for all types of synchrotron radiation, which is further enhanced in the case of an undulator [21].

Even with a high-brightness source like an undulator, the problem of focusing the X-ray beam remains quite difficult for radiation in the soft-X-ray range which is typically used in spectromicroscopy, $h\nu$ = 10-1,500 eV. This is due to the fact that materials do not transmit in this range, and poorly reflect this radiation except at grazing incidence. Therefore, its is quite difficult to fabricate focusing optical components.

The are two main solutions to this problem:

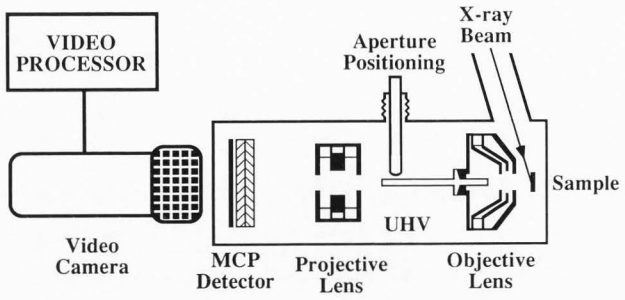

Figure 6. Scheme of Tonner's X-ray secondary electron microscope (XSEM) [27].

• **Transmission Fresnel zone plates** (see Fig. 5a): These are devices produced by electron-beam lithography [16, 17], with radiation-blocking rings ("zones") over a thin transmitting substrate. The focusing condition is $\lambda = \{D^2 + (R_{N+1})^2\}^{1/2} - 2(D^2 + R_N^2)^{1/2} \approx \{(R_{N+1})^2 - R_N^2\}/2D$, where D is the focal distance and R_N is the radius of the N-th zone, which is satisfied if $R_N = (2ND\lambda)^{1/2}$. The width of the N-th zone is of the order of $\delta R_N/2 \approx (D\lambda/8N)^{1/2}$; if Δ is the minimum zone width achievable with the electron-beam lithography technique used for fabrication, then the maximum value of N is $D\lambda/8\Delta^2$, corresponding to a zone plate radius equal to $D\lambda/2\Delta$. The minimum zone width Δ also determines [16, 17] the lateral resolution, i.e., the diffraction-limited size of the focused beam.

These results illustrate the rather severe geometry/fabrication problems affecting these devices [16, 17]. The minimum zone width typically ranges from 500-1,000 Å, although in the case of photoemission microscopy, the lateral resolution does not quite reach the lower limit of this range [16, 17]. For λ = 20 Å and Δ = 1,000 Å, the focal length is only approximately two orders of magnitude larger than the zone plate's radius; and it does not exceed a few millimeters, which corresponds to a rather small working area.

Devices of this kind have been primarily used at the Brookhaven National Synchrotron light source, and have produced interesting results for several years [16, 17].

• **Schwarzschild objectives** (see Fig. 5b): These are reflection devices consisting of two different spherical elements [25]. The main problem in this case is the limited reflection at non-grazing incidence. This problem was solved by scientists at the Lawrence Berkeley Laboratory's Center for X-ray Optics [25] by using multilayer coatings to enhance the reflectivity of the spherical surfaces.

Devices of this kind have been extensively used for the scanning photoemission spectromicroscope MAXIMUM at Wisconsin [25]. The complete focusing configuration of MAXIMUM includes a pre-focusing stage consisting of grazing-incidence mirrors, and a pinhole. The demagnified pinhole determines the lateral resolution. This instrument holds the present world record for lateral resolution in photoemission spectromicroscopy, at 900 Å (which also gives, as we have seen, the record value for the Q-parameter). This is still quite far from the ultimate diffraction limits (of the order of a few 100 Å), and the main limiting factor is still the signal level.

Electron optics and imaging techniques

In this class of spectromicroscopy techniques [27, 28, 29], the photon beam is either not focused or only partially focused, so that it floods a large area of the sample and cannot provide lateral resolution (see Fig. 1b). The photoemitted electrons are processed by an electron optical system, much like in a normal electron microscope, and then the magnified electron image is revealed by a microchannel plate, followed by a video camera connected to a video recorder. The signal level is, in fact, high enough to take images in real time. An example of system of this type, Tonner's X-ray secondary emission microscope (XSEM) [27, 28], is schematically shown in Figure 6.

The differences in the performances between this approach and scanning spectromicroscopy can be easily understood if one considers their basic complementarity. We have seen that "spectroscopy" in scanning spectromicroscopy primarily means taking electron energy distribution curves at constant photon energy. On the other hand, spectroscopy techniques that require photon energy scanning cannot be easily implemented in scanning spectromicroscopy, because the technical characteristics of the soft-X-ray focusing devices: in fact, the focal distance changes with λ for zone plates [16, 17], and the multilayer coating of a Schwarzschild lens only works in a narrow range of λ's [25].

Photon energy scanning is quite easy, on the contrary, for the electron optics-imaging approach, whereas electron energy scanning can pose problems. Therefore, the main "spectroscopy" in electron optics-imaging spectromicroscopy is the so-called partial-yield technique [12, 27, 28], in which the photoelectron yield at a given electron energy is monitored as a function of the photon energy, $h\nu$.

This technique was invented in the 1970's by Gudat and Kunz [12], and it basically is a measure of the X-ray absorption coefficient: the photoelectron yield is, in fact, proportional to the absorption of X-rays. Note, however, that photoelectrons are only emitted from a thin slab near the surface of the specimen, since their mean-free-path is of the order of angstroms or tens of angstroms [19]. Thus, partial-yield measures the X-ray absorption coefficient of the surface region [23].

The mean-free-path of the electrons depends on their energy [19], and by changing the collected electron en-

ergy one can decrease or increase the surface sensitivity as required for each particular experiment. When surface sensitivity is not an issue, one uses very low energies corresponding to the maximum of the emission of secondary photoelectrons, in order to enhance the signal level.

The electron optics-imaging approach, therefore, makes it possible to measure surface-sensitive partial-yield spectra from small areas. Furthermore, this approach can deliver micrographs taken at selected photon energies. Suppose that two micrographs are taken at energies immediately below and above an X-ray absorption edge of a given element: the comparison of the two images is an excellent way to identify and analyze the spatial distribution of that particular element. This procedure can be further enhanced by subtracting pixel-by-pixel the intensity of the two images: the resulting difference micrograph primarily reflects the spatial distribution of the element under consideration.

When comparing focusing-scanning spectromicroscopy and electron optics-imaging spectromicroscopy, we find again complementarity between the two approaches: one cannot say that one approach is "the best" for all applications. Each class of techniques performs better than the other for specific types of experiments, but the best procedure in general is a parallel and complementary use of both classes. Used together, such techniques can deliver a complete picture of the chemical, electronic-structure and optical properties of the system under investigation.

Problems in Data Taking Strategy

Before considering practical examples of photoelectron spectromicroscopy, we must discuss a rather delicate and often overlooked problem: the necessity of carefully planning the data taking (and data analysis) strategy [22]. The basic point is that without careful planning, one risks to waste time by either taking unnecessary data, or taking data in an ineffective way. A waste of time is always undesirable, because experiments of this type use expensive experimental resources of limited availability, such as advanced synchrotron facilities. The waste of time, however, could be quite marginal in the case of spectroscopy experiments, but it almost invariably becomes disastrous when moving from spectroscopy to spectromicroscopy.

We will illustrate this point with some examples and a personal recollection. The first example concerns resolution: suppose that one seeks information about the spatial distribution of a given element, discriminating between two possible oxidation states. Also, suppose that the information is sought by analyzing a given core level of that element; the energy position of the core level changes depending on the oxidation state, thus, by analyzing scanning micrographs taken at two different electron energies, one can "see" the spatial distribution of the two oxidation states.

The issue is: how much energy resolution does one need to discriminate one oxidation state from the other? The answer is given, of course, by the distance in energy between the two corresponding core-level positions: typically, an energy resolution similar to this distance is sufficient.

Suppose instead that one "overkills" the problem by using ten times more resolution than needed. This requires closing one or several slits in the photon monochomator systems, and/or their equivalent in the electron analyzer system, thereby decreasing the signal level at least by a factor of ten. In order to reach a sufficient signal level, one must increase the data accumulation time per spatial point (pixel): the "overkill" results in a waste of valuable instrumental time.

Note that one can "overkill" the lateral resolution as well as the energy resolution. Since there are two spatial coordinates, the effects could be quite dramatic. Combined "overkills" for the energy resolution and for the spatial resolution are quite likely to lead to disaster.

Suppose, for example, that a micrograph of a given specimen reveals an interesting spatial feature, and that one wants to learn about the chemical properties of this feature; also suppose that the feature only concerns 5% of the pixels of the 10^4 pixel micrograph. The correct strategy is to focus on the specific pixels of the feature, and take complete photoelectron-energy-distribution spectra from those pixels, together with 3-5 reference spectra from the rest of the pixels.

Quite often, however, one sees experimentalists adopting a brute-force approach, taking spectra from all pixels and then analyzing only those from the pixels of interest. The justification is that "one never knows" what information might be required later. This might very well be true, but the cost of taking information of uncertain usefulness is so unreasonably high that one is forced to take some risks!

Suppose, in fact, that the data taking time per spectrum is 1 minute. The total time for the 5% pixels corresponding to the interesting spatial feature is 500 minutes, already more than 8 hours! Without discrimination, the total time for 10^4 pixels becomes almost 170 hours, of which some 160 are wasted, a synchrotron beam-time cost of up to 80,000 US dollars. Clearly, careful data-taking planning is not an option but an absolute necessity for spectromicroscopy.

The point is that "spectroscopy" is typically an one-dimensional technique, in which "spectra" are taken as a function of only one variable, such as, the electron or the photon energy, whereas "spectromicroscopy" is a

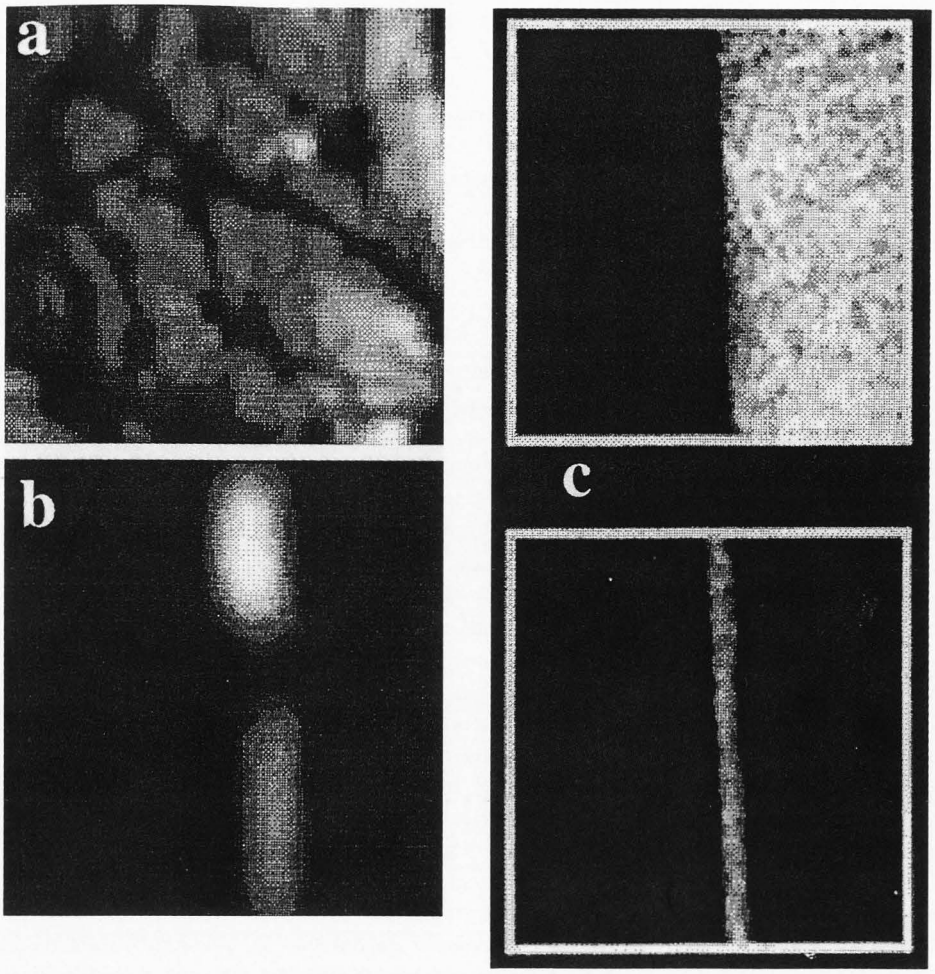

Figure 7. Scanning photoelectron spectromicroscopy micrographs: (**a**) a neuron culture from De Stasio *et al.* [7] (image size 80 x 80 μm^2); (**b**) a GaAs-(Ga,In)As heterojunction: in this case, the intensity of an indium core level reveals the spatial distribution of this element [25] (image size 20 x 20 μm^2); (**c**) a GaAs-GaAs homojunction [25] (image size 12 x 12 μm^2): in this case, there is no chemical contrast; however, the p-n character of the homojunction produces an electrostatic shift between the electronic states of the two sides of the junction; this explains the change in contrast between the two images, taken at two different photoelectron energies.

three-dimensional technique with one energy variable and two spatial coordinates. Therefore, a small mistake in strategy could cost a negligible waste of time in "spectroscopy", but become a disaster in the corresponding spectromicroscopy. The data taking strategy must be analyzed with sophisticated methods in the latter case [22].

Note that this problem is not confined to spectromicroscopy alone. A similar problem occurs when photoemission spectroscopy is performed with high angular resolution [19], and the direction coordinates play a role. The practitioners of angle-resolved photoemission know that angle-resolved spectra are typically taken along specific high-symmetry directions of the crystallographic structure of the sample under investigation. This is justified by the fact that theoretical band-structure calculations are also performed along high symmetry directions, so that a comparison between theory and experiment can only be performed for such directions.

There is, however, another problem that makes it impossible to take data in all directions: the waste of time. This author remembers that in the early days of angle-resolved photoemission with synchrotron radiation, the IBM and Bell Labs.-Wisconsin groups operating at the Wisconsin Synchrotron Radiation Center simultaneously commissioned two powerful systems, capable of taking photoelectron spectra along many different directions in parallel. A competition developed between the two groups, which tried every day to reach new records in the total number of spectra.

This produced literally hundreds of thousands of spectra. In retrospect, however, only a small portion of these spectra was utilized, since electronic band mapping could be theoretically tested only along the aforementioned high symmetry lines. In those happy days, the synchrotron beam-time was still relatively inexpensive, so that the two groups (this authors was a member of the second) did not have to pay for the wasted time. Today, the consequences could be much more dramatic!

What are, therefore, the elements of an intelligent data taking strategy? This problem has been analyzed in some detail, using an information-entropy approach [22], and we present here only some of the basic conclusions:

- The first general rule is that one has to decide *a priori* what type of information one seeks from the experiment, and develop the data taking strategy to

obtain that information and nothing else.

- Based on the sought information, the spatial and energy resolution levels must be selected in order to optimize the information content of the spectra. The "maximum extractable information" [22] from a spectrum or from an image is determined by the interplay of resolution and of the signal-to-noise level: excessive resolution decreases the "maximum extractable information" because it negatively affects the signal-to-noise level. As a general rule, the "maximum extractable information" is optimized when the resolution is comparable to the "size" of the features that one must detect [22]. For example, if in an image one tries to determine the position a dot of diameter d, the spatial resolution which optimizes the image's information content is also $\approx$ d. Similarly, if one tries to measure the energy spectral position of a peak whose intrinsic width is δE, the optimum resolution is also $\approx \delta$E.
- The data-taking strategy changes from one mode of spectromicroscopy to another, therefore, one cannot develop a general-purpose strategy. A specific analysis must be performed for each specific experiment [22].
- Errors in the data-taking strategy in spectromicroscopy cannot be compensated by increasing the data-taking time, because of the high cost of the use of the instrumentation. This is true, in particular, for the experiments requiring high-quality synchrotron radiation beam-time, such as undulator beam-time.
- Common-sense planning based on intuitions can be helpful in some simple cases, but it could lead to an incorrect analysis in other cases, and to potential strategic disasters. A rigorous analysis is always safer [22].

In a sense, therefore, spectromicroscopy with high-cost instruments forces the experimentalists to deal with engineering and cost-analysis problems that are not commonly found in conventional laboratory practice. The usual academic opinion that time and labor (graduate students) costs can be neglected clashes in this case with the reality of the high cost of centralized instrumentation.

Examples: Scanning Photoelectron Spectromicroscopy

A complete review of the many results already produced by spectromicroscopy is well beyond the scope of this presentation: we will only discuss a limited number of cases, to exemplify what can be accomplished with these novel techniques, beginning with scanning spectromicroscopy. The examples have been specifically selected to illustrate the different factors in the image formation process.

Figure 7 shows several scanning photoelectron micrographs taken at MAXIMUM, with contributions from different image formation mechanisms. In Figure 7a, we see the image of a portion of a neuron culture on a metallic substrate [7]; in this case, there are primarily two image formation factors: chemical contrast and topography. The image was taken by detecting secondary electrons, so the chemical contrast is not linked to the detection of a particular core level of a particular element, but to the overall difference in secondary photoelectron emission for different chemical elements.

As to topography, it is well known that primary photoelectrons may have strongly anisotropic angular distributions with respect to the emitting surface [19]. Similar, although more moderate, anisotropies may exist for the secondary electrons. Topography can influence the local orientation of the emitting surface, and therefore, the photoelectron intensity collected by the electron analyzer, which samples only a portion of the possible directions of photoelectron emission.

The chemical-contrast factor is quite evident in Figure 7b, where we see the transverse micrograph of a GaAs-(Ga,In)As heterojunction [25]. The micrograph was taken by detecting photoelectrons originating from a core level of indium, therefore the intensity reveals regions where indium is present.

Figure 7c illustrates yet another image formation mechanism [25]. The contrast between the two sides, which is reversed by changing the detected photoelectron energy, cannot be related to chemical differences, because we are dealing here with a GaAs-GaAs homojunction with the same elements on both sides. On the other hand, the p-n character of the junction causes a difference between the electronic energy positions of its two sides. By properly tuning the detected electron energy, one can capture core-level photoelectrons originating from either the "p" or the "n" side of the junction, thereby changing the contrast.

The spectroscopic capabilities of focusing-scanning spectromicroscopy are illustrated by Figure 8. We see in Figure 8a a micrograph of a thin (0.5 monolayer, ML) germanium overlayer deposited on a GaSe substrate [11]. The image reveals a potentially interesting linear feature: what is its nature? This question was explored by comparing core-level photoelectron spectra taken on the feature and those taken elsewhere [3]. It is quite clear from Figure 8b that the Ge core level does not appreciably change between the two locations, so the difference is not due to a different chemical status of the overlayer element.

On the other hand, Figures 8c and 8d clearly reveal significant shifts for the Ga and Se core levels of the substrate. The shifts have the same value and the same direction for Ga and Se. Therefore, they are not due to a difference between the two location as far as the chemical status of these elements is concerned. The most probable cause is a difference in the substrate band bending between the two locations, which produces the

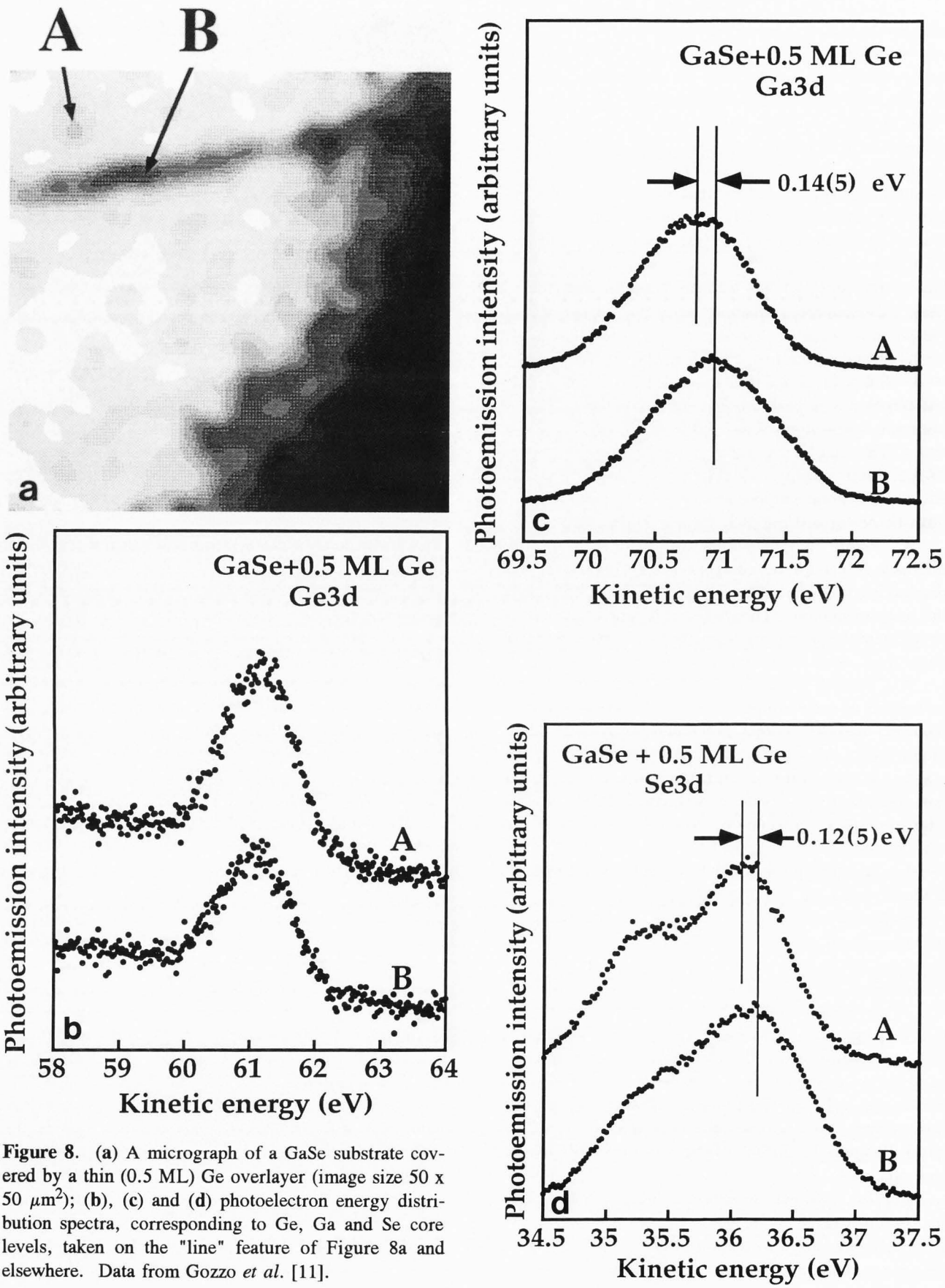

Figure 8. (**a**) A micrograph of a GaSe substrate covered by a thin (0.5 ML) Ge overlayer (image size 50 x 50 μm^2); (**b**), (**c**) and (**d**) photoelectron energy distribution spectra, corresponding to Ge, Ga and Se core levels, taken on the "line" feature of Figure 8a and elsewhere. Data from Gozzo *et al.* [11].

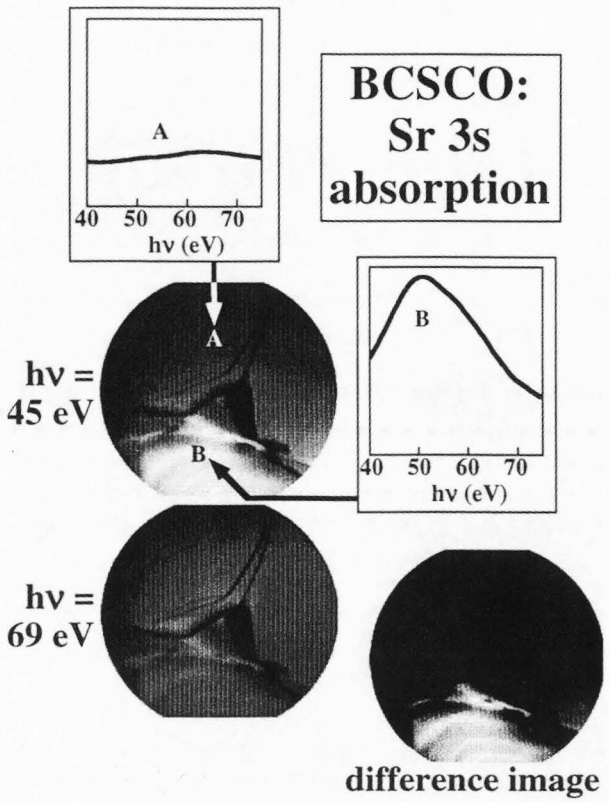

Figure 9. An electron optics-imaging study of the chemical composition of a high-temperature superconducting BCSCO-2212 specimen. We see two micrographs (size 240 μm) at left, taken at two different photon energies in the spectral range of a Sr X-ray absorption edge, plus their pixel-by-pixel difference (bottom right). Spatial features that do not depend on hν are of topographic origin; in addition, we see an area with hν-dependent intensity. A comparison of partial-yield (X-ray absorption) spectra taken inside (A, top left) and outside (B, middle right) the area reveals in this latter an excess amount of Sr. The difference image emphasizes the spatial distribution of the excess Sr. The results are from the first spectromicroscopy experiment at the SRRC facility in Hsinchu, Taiwan [13].

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same electrostatic shift for all spectroscopic features of all elements [11].

This is an interesting result [11], since the invariance of the Ge peak and the shift of the Ga and Se peaks implies a different lineup of the two band structures of the two sides of the junction. This suggests that the band lineup is not a common property of all parts of the interfaces, but can change from place to place. Results of this kind have been found for other semiconductor interface parameters, such as the band bending of semiconductor-vacuum interfaces [2] and Schottky barriers [10], and are forcing a revision of accepted notions in semiconductor interface physics.

Examples: Electron Optics-Imaging Photoelectron Spectromicroscopy

We will now illustrate with some examples the capabilities of electron optics-imaging photoelectron spectromicroscopy. Figure 9 shows a nice example of the different types of image formation mechanisms. We see the contrast of two micrographs taken with the STAIB photoelectron emission microscope (PEEM) instrument on the SRRC source in Hsinchu, Taiwan [13]. The micrographs were taken on a single-crystal surface of a BCSCO-2212 high-temperature superconductor, using two different photon energies. Such energies were selected in a spectral region including a strontium X-ray absorption edge.

We see that some features do not change with the photon energy: these are most likely topographic features, not related to chemical contrast. On the other hand, we also see a marked difference between the intensity of a specific area in the two micrographs. The cause is quite clear if one compares photoelectron yield (X-ray absorption) spectra taken inside and outside the area: inside, one sees the strontium edge, whereas outside one does not. This means that the area corresponds to an anomalous high concentration of strontium, probably due to a microprecipitate.

The pixel-by-pixel subtraction image in Figure 9 clearly reveals the localized distribution of the suspected microprecipitate. Note that microprecipitates are quite unlikely to occur in these specimens: a very few cases were detected in the spectromicroscopy analysis of Figure 9, and no cases in extensive microprobe tests.

This approach is now routinely used to assess the local chemical composition and the quality of single crystals manufactured for spectroscopic applications. A similar approach has been used to empirically relate the local chemistry and the local response of cesium oxide particle detectors, thereby paving the way for a better fabrication recipe and for an increase in efficiency by a factor ≈ 2 [5].

Perhaps the most spectacular results with this technique have been obtained in the study of neurobiological specimens [9]. Two points must be noted: first of all, the recent lateral resolution in the submicrometer range finally enables photoemission techniques to make contributions in the life sciences, whose specimens must be studied on the microscopic scale of cells and cell components. Second, the high signal level in electron optics-imaging spectromicroscopy makes it possible to quickly survey large specimen areas, looking for traces of a given element.

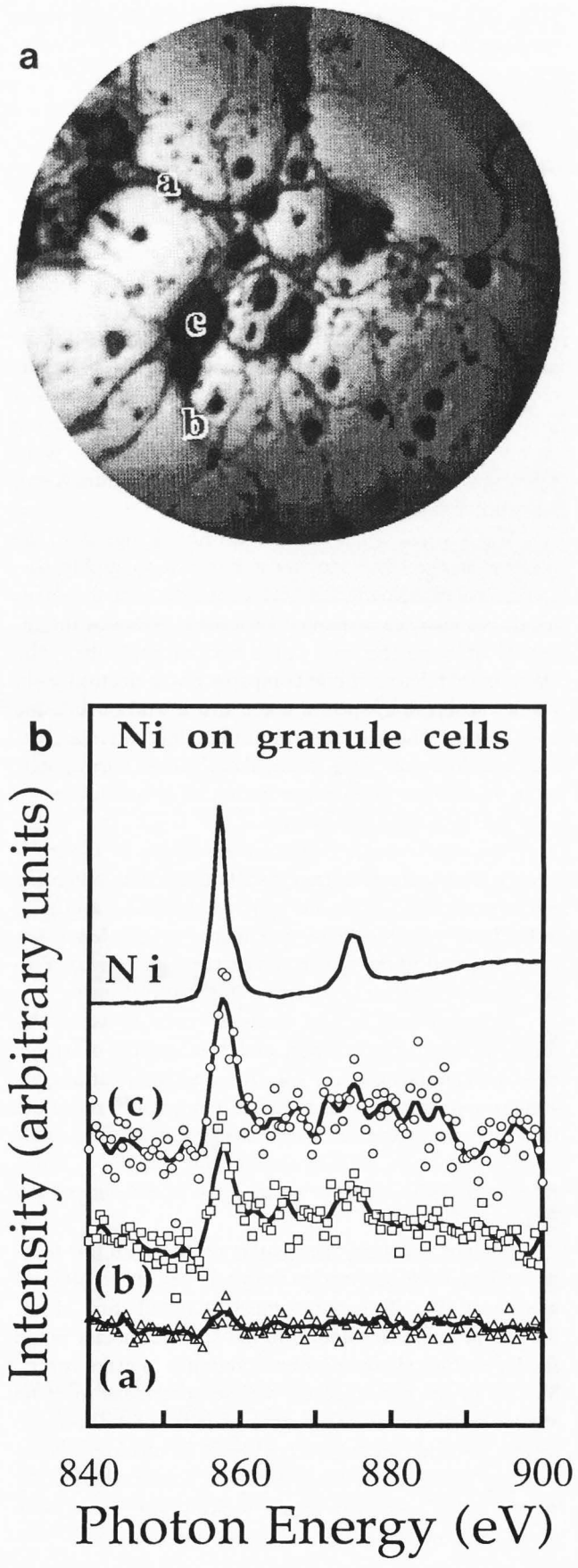

Figure 10. (**a**) XSEM [27] micrograph of a neuron culture, after exposure to nickel (size = 50 μm); (**b**) partial-yield (X-ray absorption) spectra from different points in the micrograph, plus a reference spectrum showing a nickel absorption edge. Data from De Stasio *et al.* [9].

This capability has been extensively used to study the spatial distribution of toxic elements in neurobiological specimens. For example, a survey of 10^5 cells, primarily granule neuron cells, after exposure to aluminum revealed this element in only three cells, all non-granules [8]. This potentially interesting result has been repeatedly verified, for example by detecting an anomalous high aluminum content in cultures primarily consisting of non-granule cells [9].

Figure 10 shows a nice example of microchemical analysis of a neuron culture specimen using this approach [9]. Figure 10a presents a micrograph taken with Tonner's XSEM on a culture after exposure to nickel; Figure 10b shows a series of partial-yield (X-ray absorption) spectra from different points in Figure 10, in the spectral region of a nickel absorption edge [9]. The differences in nickel uptake from place to place are quite evident.

Very Recent Developments and Future Possibilities: the Free Electron Laser

The major development in this novel area is the recent commissioning of the first synchrotron sources of the third generation, characterized by a extremely high level of brightness. Figure 9 shows an example of data produced by one of these sources: SRRC in Taiwan [13]. The other members of this limited group are ELETTRA in Trieste, the ALS at Berkeley, the Pohang facility in South Korea, and for hard X-rays, the European Synchrotron Radiation Facility in Grenoble.

Spectromicroscopy is one of the best ways to take advantage of the higher brightness level, as we have realized from the discussion of the role of undulators in focusing-scanning techniques. The electron optics-imaging approach also profit from higher brightness because of the increase in signal level.

It is not surprising, therefore, that microscopy and spectromicroscopy constitute a substantial fraction of the planned applications of the new synchrotron sources. The results of Figure 9 were one of the very first experiments on SRRC-Taiwan [13]. In the case of ELETTRA, the inaugural experiment [1] was performed with a PEEM instrument; Figure 11 shows one of the corresponding micrographs [1].

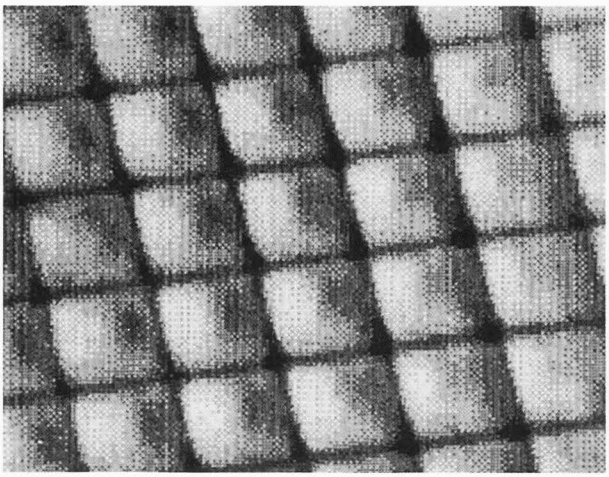

Figure 11. PEEM micrograph of a metal mesh, from the inaugural experiment of the ultrabright synchrotron source ELETTRA in Trieste [1]. The size of the figure is 110 x 95 μm.

Can we increase the brightness level beyond what is possible with the recently commissioned synchrotron sources? Some ideas have been formulated in that direction, for example in the context of the Swiss Light Source (SLS) [30] proposal. There is no question that this field could use an additional increase in brightness, in order to reach the diffraction limits for lateral resolution, and combine them with more advanced energy resolution, perhaps the 10-20 meV level currently used in photoelectron spectroscopy to study collective phenomena in high-temperature superconductors and other materials [18]. Furthermore, higher brightness could make it easier to implement novel approaches, perhaps technical solutions linked to near-field microscopy.

There might exist one simple way to improve the effective brightness even before building a new generation of synchrotron sources: the use of undulator beamlines without monochromators. We have seen that an undulator emits radiation in a narrow bandwidth of wavelengths, therefore, it is *per se* a monochromator with resolving power $\lambda/\delta\lambda = n$, the number of periods. Normally, n is limited to less than 20-30 periods, and the resolving power is not sufficient for spectroscopy, so that a monochromator is added to the beam-line for additional filtering. This, however, causes a loss in intensity and therefore in the effective brightness delivered to the sample chamber.

Could one improve the undulator's $\lambda/\Delta\lambda$ and eliminate the monochromator, thereby increasing by orders of magnitude the effective brightness of the beam-line? The answer is a qualified yes. On one hand, the magnet technology has sufficiently evolved to build undulators with a large number of periods. On the other hand, beyond a certain value of n, the relation $\lambda/\Delta\lambda = n$ is no longer valid, and the bandwidth $\Delta\lambda$ is determined by a different mechanism.

This mechanism is related to the energy of the electron beam passing through the undulator. We have seen that the emitted wavelength (eq. 3) is $\lambda \approx L/2\gamma^2$, where γ is the energy of the electron beam in units of the electron's rest energy, m_0c^2. In practice, however, γ is an average value, since the electrons in the beam have a finite energy spread, $\delta\gamma$. This is an intrinsic phenomenon for electrons in a synchrotron source, since the energy spread is caused by the very emission of synchrotron radiation photons.

The energy spread $\delta\gamma$ causes a spread in the emitted wavelength $\gamma \approx L/2\gamma^2$, of the order of $2\lambda\ \delta\gamma$. When the number of periods is already so high that the corresponding bandwidth $\delta\gamma/n$ is smaller than $2\lambda\ \delta\gamma$, one no longer gains in resolution by further increasing n.

For practical cases, this sets a maximum limit of the order of $\lambda/\delta\gamma = n = 100\text{-}200$ for the intrinsic resolving power of an undulator. This is at the same time bad news and good news: for most spectroscopy experiments, this resolving power is not sufficient, and one must use a monochromator with the corresponding loss in effective brightness. On the other hand, a resolving power of 100-200 is sufficient for many of the experiments in spectromicroscopy. For example, it is typically largely sufficient to distinguish different elements, and in some cases, even to distinguish different oxidation states of the same element. One can, therefore, foresee specialized spectromicroscopy beam-lines, with long undulators and no monochromators, perhaps dedicated to very fast experiments in real time.

We would like to conclude this presentation by mentioning yet another type of spectromicroscopy under development, based on the so-called free electron lasers (FEL's) [4, 24]. These are sources in the same general family as the synchrotron radiation facilities, in the sense that they are based on a similar electron accelerator technology. In a normal laser, the lasing action is due to stimulated emission in a medium which can be a solid, a gas, or a liquid. In an FEL, the medium is a bunch of "free" electrons that interact with a periodic array of magnets, like a wiggler.

We have seen that the undulator-electron interaction leads to spontaneous emission of photons of wavelength $\approx L/2\gamma^2$. The FEL uses a similar phenomenon of stimulated emission at the same wavelength. The gain is enhanced with an optical cavity, and can allow a lasing action. Unfortunately, the gain decreases with the wavelength, so that the FEL's work much more easily in the infrared than in the ultraviolet or X-ray ranges.

Several FEL's have been developed in the world, and they can provide excellent intensity coupled to broad-band tunability in the infrared. These sources find interesting applications in diverse branches, ranging from materials science to medical research. In materials science, for example, they have been used to measure with high accuracy and reliability, interface energy barriers of semiconductor devices [4, 24].

Recently, a major effort has been initiated to add lateral resolution to these FEL applications, thereby developing a novel FEL spectromicroscopy. The effort is primarily based on optics fibers and a near-field-optics approach. No FEL results have been obtained yet, but they can be expected during the next 18 months.

This novel technique, therefore, is likely to further expand the already rich arsenal of spectromicroscopy. We have seen how spectromicroscopy brings for the first time in the submicrometer domain the outstanding analytical capabilities of spectroscopies like photoemission, thereby opening up new opportunities for chemical and physical analysis on a microscopic scale. Other spectroscopies, besides photoemission, can evolve into spectromicroscopy, and this has already happened in several cases (notably for fluorescence spectroscopy). We can foresee, therefore, the development of a powerful array of new investigation methods in materials science and the life science. The only limitation to their applications is the creativity of the interested scientists.

Acknowledgments

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Discussion with Reviewers

Reviewer IV: State of the art EELS imaging has yielded energy resolved data with a spatial resolution of less than 1 nm, which yields a quality factor Q easily an order of magnitude larger than that for the STM. Yet, the STM has been used as the high extreme limit on this Q scale and forms the basis of the comparison of the capabilities of X-ray spectromicroscopy. It would seem rather educational to include EELS work. Could you comment on this omission?

Author: As shown in the text, EELS should indeed be used as a reference together with the STM; the referee is correct in that regard. I note, however, that EELS, as a spectroscopy technique, has severe limitations in comparison to photoelectron spectroscopy, most notably as far as the complexity of data interpretation, the power of chemical analysis (including chemical status) and the modification of the analyzed system by the primary beam are concerned. These limitations are likely to be mirrored in the spectromicroscopy versions of the two techniques.