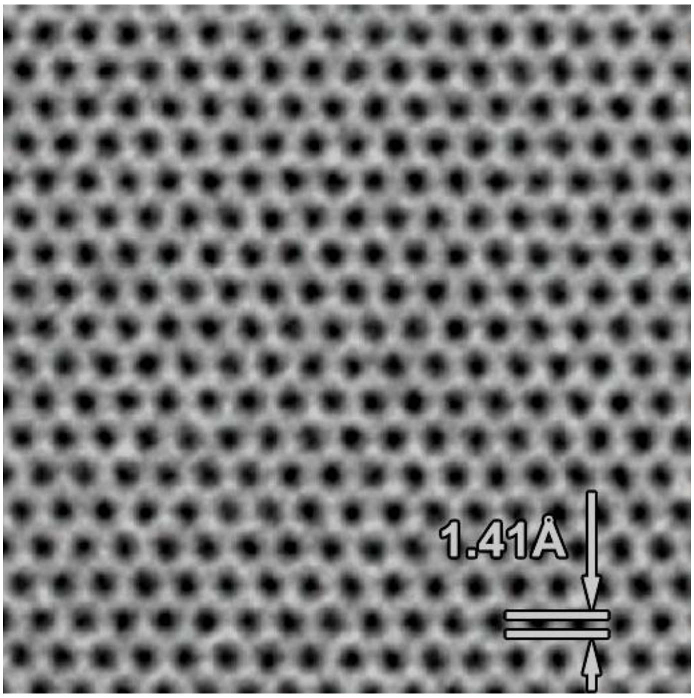
Д.А. Кириленко

DIRECT TECHNIQUES OF STRUCTURE INVESTIGATION



Санкт-Петербург
2023

МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ
РОССИЙСКОЙ ФЕДЕРАЦИИ

УНИВЕРСИТЕТ ИТМО

Д.А. Кириленко

DIRECT TECHNIQUES OF STRUCTURE INVESTIGATION

УЧЕБНО-МЕТОДИЧЕСКОЕ ПОСОБИЕ

РЕКОМЕНДОВАНО К ИСПОЛЬЗОВАНИЮ В УНИВЕРСИТЕТЕ ИТМО
по направлению подготовки 16.04.01 Техническая физика
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Учебное пособие разработано при поддержке Министерства науки и высшего образования Российской Федерации (соглашение № 075-15-2021-1349) и предназначено для использования в качестве учебно-методического пособия в рамках реализуемых дисциплин образовательной программы «Лазерные и синхротронные технологии магесайенс/Megascience laser and synchrotron technologies». В пособии приведены теоретические справки по разделам курса.

Университет ИТМО – ведущий вуз России в области информационных и фотонных технологий, один из немногих российских вузов, получивших в 2009 году статус национального исследовательского университета. С 2013 года Университет ИТМО – участник программы повышения конкурентоспособности российских университетов среди ведущих мировых научно-образовательных центров, известной как проект «5 в 100». Цель Университета ИТМО – становление исследовательского университета мирового уровня, предпринимательского по типу, ориентированного на интернационализацию всех направлений деятельности.

Content

1. Introduction

Modern structure investigation techniques are rather complex and can be even considered as separate branches of natural sciences. Introduction to the presented set of methods is necessary for the specialist to be acquainted with the state-of-art abilities of the contemporary instrumentation and to be able to select properly a technique for certain tasks. The course «Direct Techniques of Structure Investigation» is intended to provide knowledge on electron microscopy and scanning tunneling and atomic-probe microscopy as a result (giving competences PK-2 and PK-5).

This teaching aid can be used for deeper study of a covered material as well as for preparation for next lectures.

2. Transmission electron microscopy

The resolution of microscopes is limited by the wavelength of the radiation used. There is a so-called *diffraction limit* of resolution or *Abbe limit*, that is the image of point source will always be blurred to size of the radiation wavelength. This does not allow resolving sufficiently small details, which is strictly consistent with the fact that it is not possible to focus a beam to a point significantly smaller than its wavelength. The reason for this is fundamental and is a consequence of the waves’ propagation physics.

The microworld came into use with the creation of optical microscopes, devices in which the human eye acts as an image detector. The native resolution of the eye as an optical device is 50-100 microns, but can be improved many times over when amplified by appropriate optical systems. The development of optical microscopy made it possible to make a number of discoveries of fundamental importance, especially in the field of biology due to the possibility of observing micro-objects such as cells, in particular bacteria, and even studying their internal structure. However, optical microscopy did not allow direct observation of the atomic structure of matter, since the wavelength of light in the visible range is 400-700 nm, which is thousands of times greater than the characteristic interatomic distances (1.5-2.5 Å).

By the beginning of the 20th century, the resolution of optical microscopes reached its fundamental limit of hundreds of nanometers, and further development of microscopy could have stalled for a long time if not for the development of quantum mechanics, which asserted the presence of a wave nature in any particles. A short time after the publication of de Broglie's formula $\lambda = \frac{h}{p}$, the first electron microscope was created, the idea of which is based on the fact that electrons in the region of practically significant energies have an essentially shorter wavelength than photons due to the presence of a rest mass for electrons (Figure 1.1).

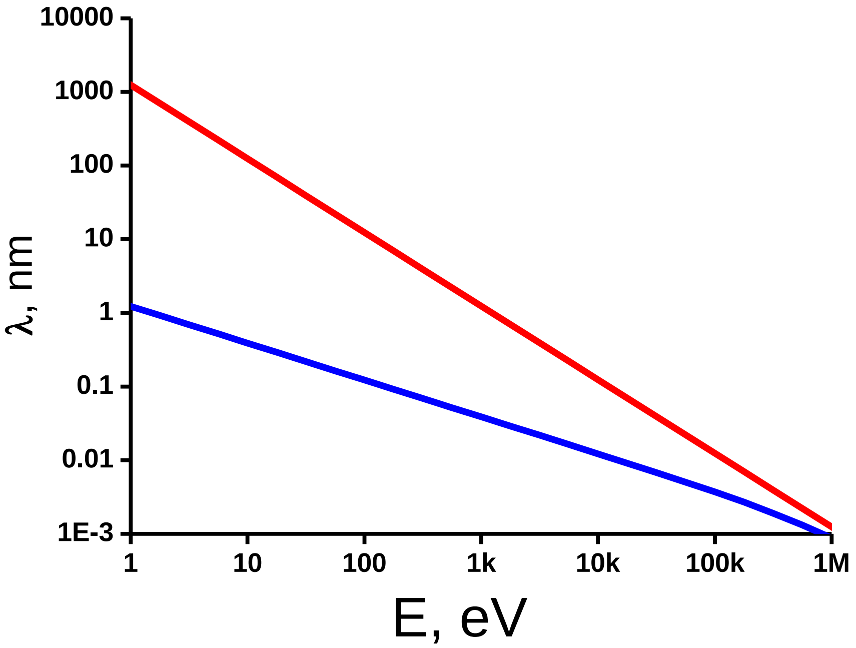


Figure 1.1 – Energy dependence of the wavelength of photons (red) and electrons (blue).

The difference in wavelengths between photons and electrons is easy to illustrate. At energies of the order of 2-3 eV, the electron wavelength corresponds to the size of the atoms and, accordingly, to the interatomic distances (~ 1Å), since these quantities are determined precisely by the electron wavelength at the characteristic energies of electronic bonds of exactly the same order. At the same time, the wavelength of photons emitted when the state of external electrons changes lies in the vicinity of the visible range, that is, 0.5 microns, which is several orders of magnitude greater than the wavelength of electrons at the same energies. In the ultrarelativistic limit, the wavelength dependences for electrons and photons converge, but this convergence occurs at energies significantly higher than the electron rest energy of 511 keV.

In practice, electron microscopes typically use accelerating voltages from 10 keV to 400 keV, which corresponds to electron wavelengths of 0.1 Å and 0.01 Å. The use of radiation with a wavelength that is many times shorter than the characteristic interatomic distances is sure to eliminate fundamental restrictions on the path to direct observation of the structure of matter.

The first electron microscope was designed and constructed in 1931 by Ernst Ruska and Thomas Knoll (Figure 1.2). For the creation of the electron microscope, Ernst Ruska was awarded the Nobel Prize in Physics in 1986. Soon after its creation, it was possible to achieve a resolution of 100 nm and thus significantly surpass existing optical microscopes.

Figure 1.2 – Ernst Ruska and Thomas Knoll at the first electron microscope (Max-Planck-Gesellschaft: [web-site]. URL: https://www.nobel.mpg.de/en/faster-smaller-more-precise).

The schematic diagram of the first electron microscopes repeats the classical optical microscope for studying biological objects, when light passes through a thin section of a sample. Electron microscopes of this type are called *transmission electron microscopes (TEM)*.

Unlike optical microscopes, electron microscopes are usually larger devices; as a result, the classic way with illumination of the sample from below and observation from above, as in tabletop microscopes, is not entirely appropriate. For this reason, the TEM circuit diagram is inverted from top to bottom compared to a conventional microscope.

At the top there is a radiation source – an electron gun. This is followed by a system of lenses that forms a beam that illuminates the sample, *an illumination system*. Initially, the size of the source in electron microscopes was relatively large (about 100 μm) compared to the size of the areas that, given the sufficiently high resolution of the microscope, could be fit in one image, so the main task of the illumination system was to reduce the size of the illuminating beam on the sample. Therefore, the lenses of the lighting system are called *condenser lenses*.

The beam then hits the sample, which is placed approximately in the middle of the microscope column. When an electron beam passes through a sample, an image is formed that carries information about the structure of the object. Directly near the object there is *an objective lens*, which forms a pre-magnified image, and performs the functions of the final condenser lens in some instruments. Then the image is magnified many times with a series of additional lenses (up to ×1,000,000) so that the human eye can analyze the resulting information. The final lens that directly projects the final image onto the corresponding screen is called *a projective lens*. The microscope also includes a complex vacuum system and electronic control units for the column elements. The classic TEM design has not changed over the past decades (Figure 1.3).

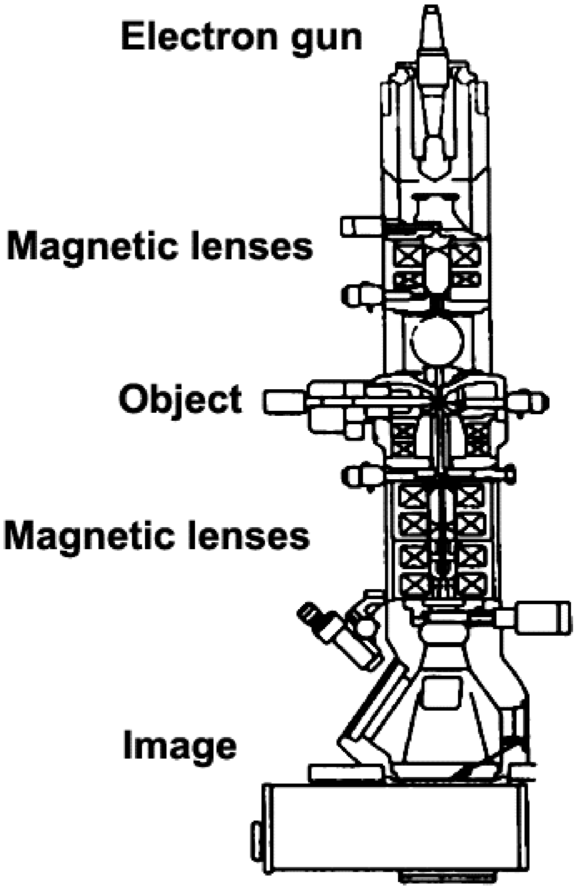


Figure 1.3 – TEM diagram.

Replacing photons with electrons allowed for a significant increase in resolution, however, it took two years for TEM pioneers to achieve a resolution of 50 nm and thus significantly surpass existing optical microscopes. Through the efforts of generations of scientists, TEM resolution reached 2 Å and allowed to observe the structure of most crystalline materials only in the 1980s. In modern microscopes, the characteristic resolution is about 0.5 Å = 50 pm, which makes TEM one of the most serious methods for studying the structure of materials, but still many times exceeds the diffraction limit ($\propto 1 - 10$ pm).

The reason for this is as follows. Electrons have a charge, which provides a number of advantages, the ability to remotely manipulate electron beams through electromagnetic fields, and also provides a relatively strong interaction of electrons with matter, which makes it possible to obtain images of even individual atoms.

However, electrons having a charge makes practically impossible to create material lenses for electrons due to their strong absorption by matter. The penetration depth of fast electrons in most materials does not exceed several micrometers, while the effective refractive index is close to unity, since the increase in the speed of high-energy electrons by the average potential of the substance is extremely small.

Electron microscopes use magnetic lenses (it is also possible to use electrostatic lenses, but over time this has been practically abandoned). The main thing that distinguishes them from material lenses is that it is impossible to create a magnetic field of arbitrary shape in a vacuum. By creating a magnetic field, we, in fact, set boundary conditions on the surface of the lens elements. The profile of the field itself along the path of electrons is already determined by Maxwell's equations, which significantly reduces the possibility of constructing fields of the desired shape. For this reason, magnetic lenses are very poor lenses when compared to their optical counterparts. For example, their spherical aberration coefficient C_s is close in value to the focal length f, that is, these lenses are applicable as optical elements in much the same way as a glass ball can be used as a magnifying glass. In optics, through the use of glass lenses it is possible to make lenses of arbitrary shape and, by varying their composition, to create almost arbitrary refractive index profiles in space. Such possibilities in electron optics are extremely limited.

The magnetic lens is a magnetic coil with a core of the required shape, called *a pole piece* (Figure 1.4). Electrons moving at an angle to the optical axis of such a lens are twisted. Moreover, their rotation period does not depend on the tangential speed, that is, on the angle of movement relative to the optical axis. Thus, in the paraxial approximation, electrons emitted from one point in front of the lens are collected again at one point after the lens. The pole pieces perform the function of enhancing the field in a small area of the lens. An important feature of magnetic lenses is the ability to arbitrarily vary the focal length from zero to certain limits by changing the current in the coil.

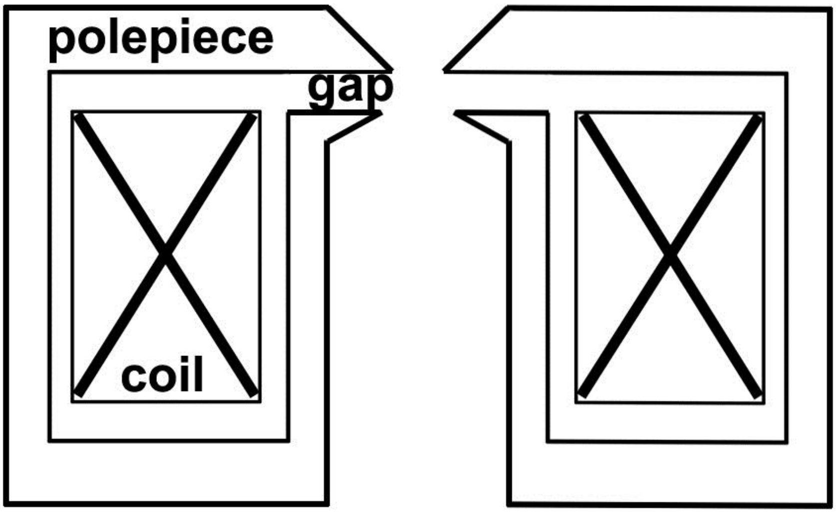


Figure 1.4 – Magnetic lens cross-section.

Since the objective lens magnifies the original image several tens of times, the influence of subsequent lenses on image quality is significantly weaker, therefore the resolution of the microscope is determined mainly by the aberrations of the objective lens and is characterized primarily by the *coefficient of spherical aberration*, measured in units of length. The spherical aberration coefficient determines the additional phase shift $\Delta\varphi = C_s\alpha^4$ of the propagating wave, where α is the propagation angle relative to the optical axis. The presence of spherical aberration of lenses does not allow focusing the image of a point source into a sufficiently small spot, the dimensions of which in an ideal case are be determined only by the diffraction limit λ/α_{max}, where α_{max} is the maximum angle of deviation from the optical axis, limited by the size of the corresponding aperture i.e. *aperture angle*. The strong dependence of the parasitic phase shift on the aperture angle limits its permissible values, which reduces the resolution of the microscope. The latter is determined by the coefficient of spherical aberration C_s of the objective lens and the electron wavelength λ according to the formula:

$$r = \sqrt[4]{C_s \lambda^3} \qquad (1.1)$$

The resolution improves significantly as the electron wavelength λ decreases, which determines the use of relatively high accelerating voltages of the order of 100 keV in TEM, while at only 10 eV it is already possible to observe individual atoms.

In 1936, Otto Scherzer showed that under the condition of axially symmetric constant field the coefficient of spherical aberration C_s of magnetic lenses is always positive. This differs significantly from the case of light optics, where it is possible to create both converging lenses with a positive coefficient and diverging lenses with negative spherical aberration and, thus, arranging lenses with practically zero spherical aberration. For many years, the development of TEM followed the path of decreasing C_s by decreasing the focal length of the lens itself, that is, by increasing the magnetic field strength. However, the ability to increase the current in the lenses is limited by stability requirements, which allowed to achieve a resolution of only about 2 Å.

At the end of the 20th century, it was shown that non-axisymmetric field configurations are possible, which have the effect of negative spherical aberration. Based on these ideas, correctors for the spherical aberration of an objective lens (C_s-correctors) were created, which made it possible to improve the resolution to 0.5 Å. Further improvement is possible by cooling the entire device to cryotemperatures to reduce thermal fluctuations in currents and voltages.

The output wave arises when the electron beam passes through the sample, which carry information about the structure of the object and is its electronic image. This image is enlarged many times with some loss of resolution and is recorded on a photographic plate or digital camera and can also be observed on a fluorescent screen.

The contrast in the image is determined by the difference in absorption and scattering of areas of the sample that have different elemental compositions. The cross sections for elastic scattering by heavier elements are significantly higher ($\propto Z^2$). In addition, the cross sections for inelastic processes are significantly higher due to the larger number of electrons in such atoms. This causes denser areas to appear darker in images (Figure 1.5).

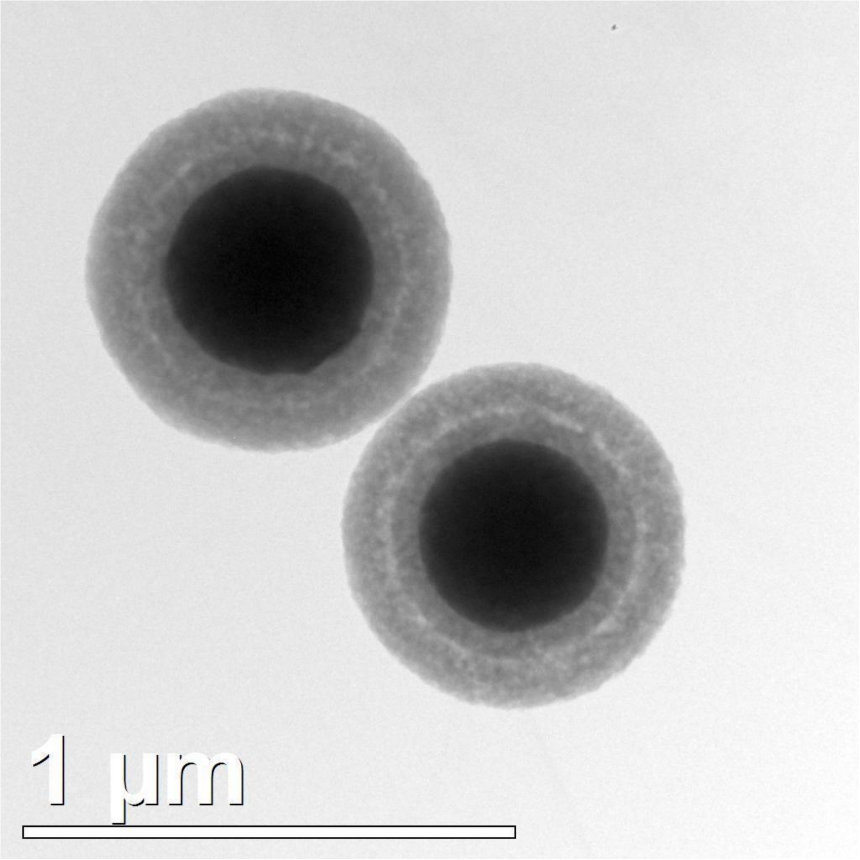


Figure 1.5 – “Core-shell” particles.

The obvious significant superiority of electron microscopy in spatial resolution determines its widespread use in structural diagnostics. However, due to the relatively strong absorption and scattering of electrons by the substance, the thickness of the material under study should not exceed 1 micron or even be much smaller.

The resolution of TEM allows to observe directly the crystalline structure of a substance as well as to detect and analyze extended defects in the crystalline structure (Figure 1.6).

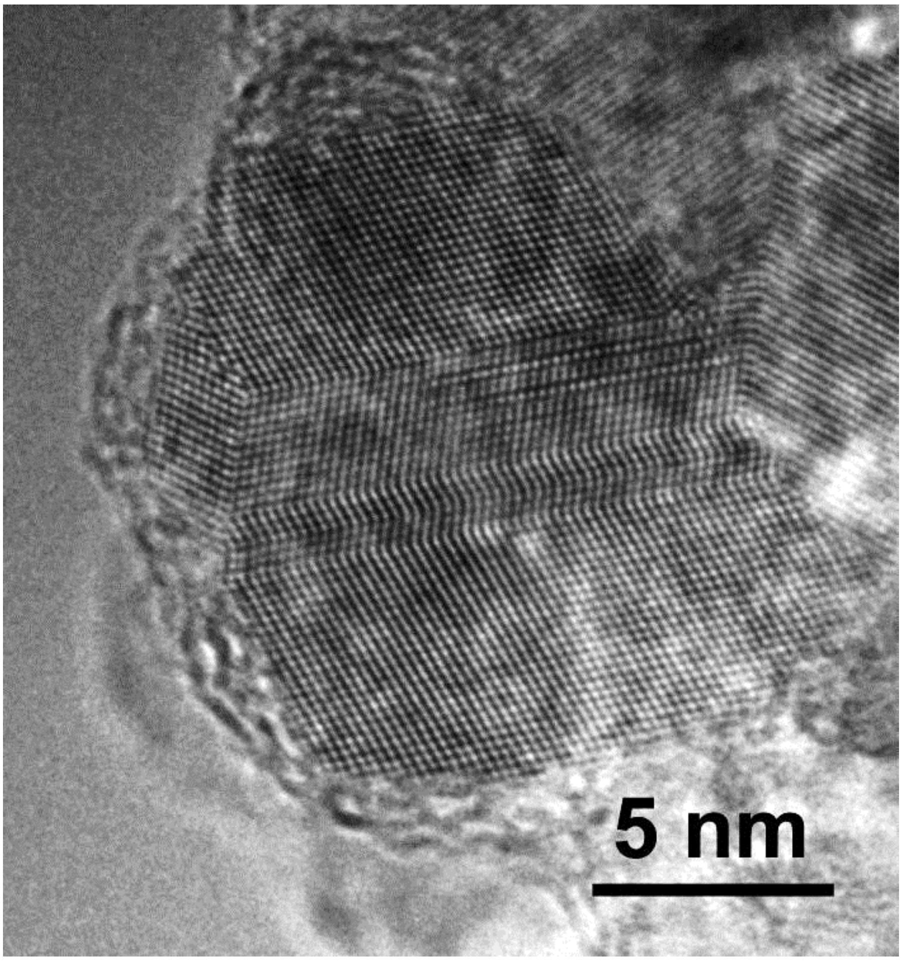


Figure 1.6 – Image of a diamond nanoparticle.

It worth noting that the resolution, that is, the degree of detail of the information provided by the method used, depends not only on the characteristics of the device, but also on the sample being studied, its elemental composition, and the geometry of the area under study. For example, TEM resolution degrades as the thickness of the region increases, as can be seen in the following image of a thin section of a multilayer structure (Figure 1.7).

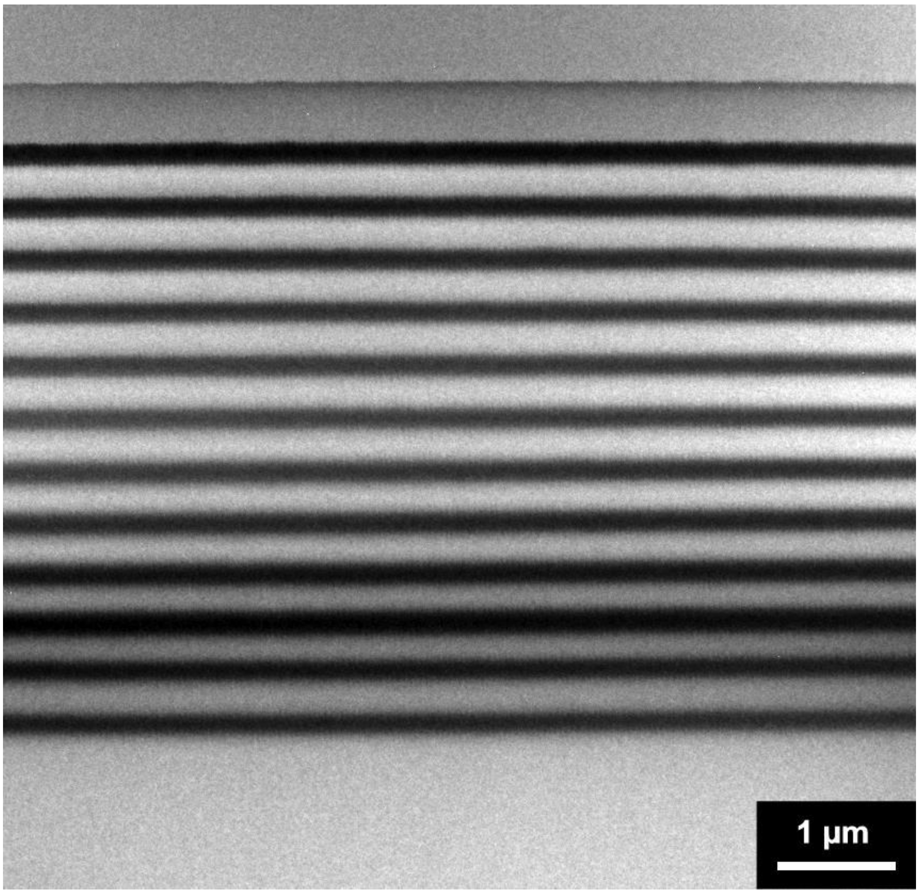


Figure 1.7 – Multilayer structure of ZrO_2 /SiO_2 .

In this image, the thickness of the slice increases as we move downward from the top edge of the structure, which can be seen from the increasing blurring of the layers boundaries in the image. Thus, to achieve TEM passport resolution, regions of <10 nm thick are required.

This resolution possible to achieve when studied nanoparticles are placed on a sufficiently thin supporting film. In this case, the thickness of the film largely determines the quality of the structural information (Figure 1.8).

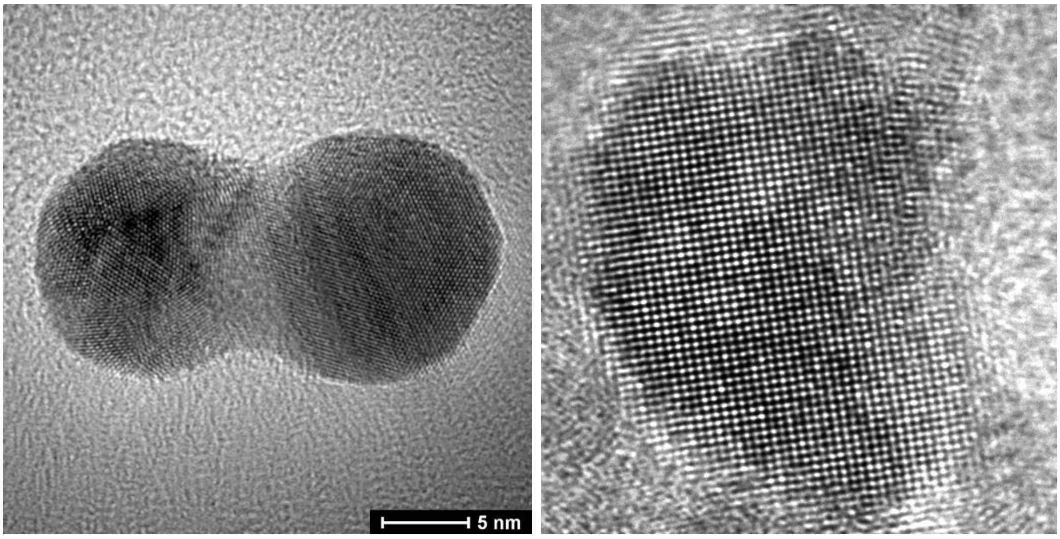


Figure 1.8 – Gold nanoparticle on a film of amorphous carbon (left) and spinel nanoparticle on a thin film of graphene oxide (right).

When studying relatively massive samples, bulk crystals or planar multilayer structures, usually grown on substrates hundreds of micrometers thick, a special technique for thinning such samples is required in order to obtain sufficiently thin sections suitable for TEM research, that is, less than 10-100 nm thick. For this purpose, ion or chemical etching, as well as mechanical nanopolishing, are most widely used, allowing to obtain areas several nanometers thick. Since these finishing processes are relatively slow, workpieces are first prepared using mechanical grinding, thinned to a thickness of about 10 microns.

Thin sections of the structure under study allow to observe its features with a sufficiently high resolution (Figure 1.9).

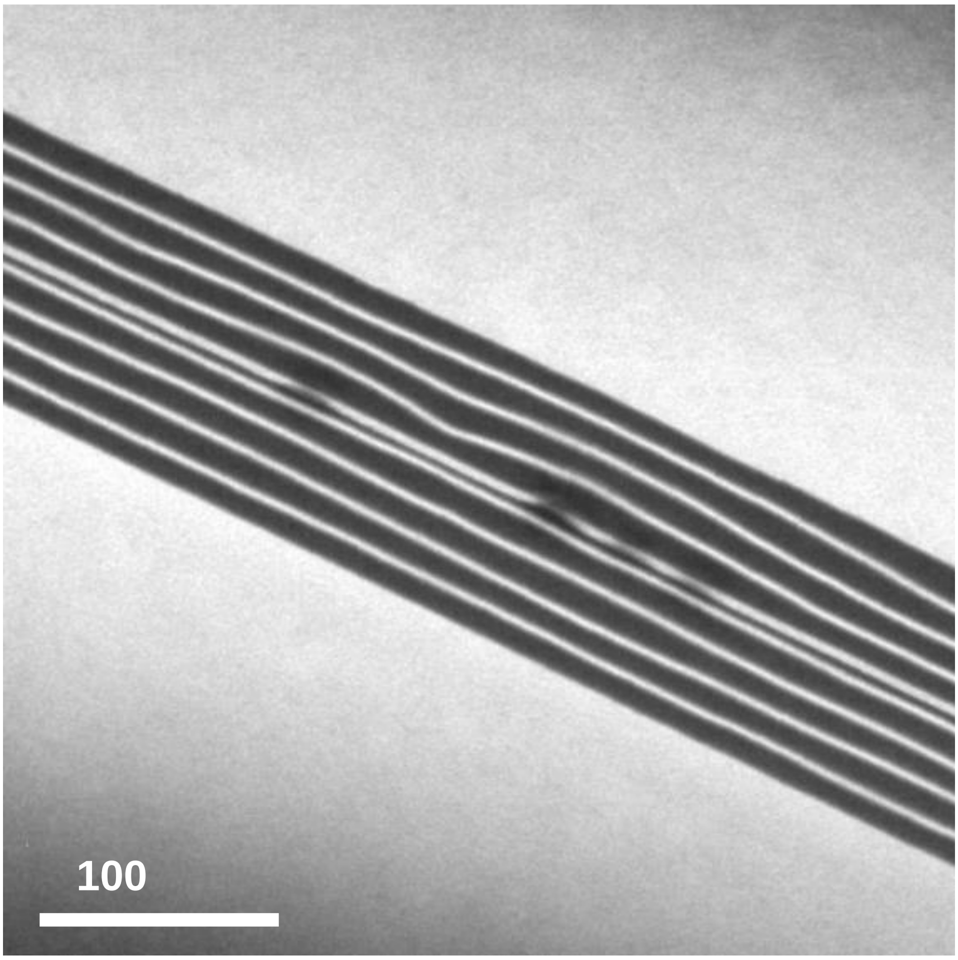


Figure 1.9 – Image of a cross-section of a multilayer structure.

The contrast in TEM images is determined not only by the electron scattering cross sections of different atoms, but also by their location in space. The difference in the structure of crystals and amorphous bodies is clearly manifested in electron diffraction patterns, since the wavelength of electrons in the TEM is much shorter than the characteristic interatomic distance (Figure 1.10).

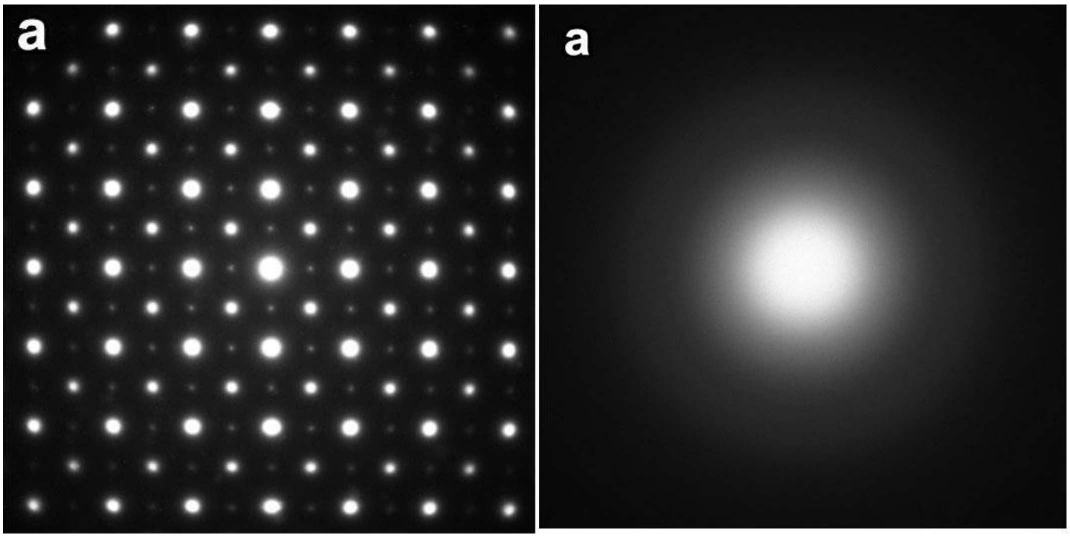


Figure 1.10 – Electron diffraction patterns on a crystal with a cubic lattice (left) and on an amorphous material (right).

Crystalline materials are characterized by a special type of electron diffraction patterns consisting bright point spots – diffraction reflections. The electron diffraction pattern represents Fraunhofer diffraction, that is, the distribution of scattering intensity across angles at a significant distance from the object. To some approximation, such a picture is described by the Fourier transform of the distribution of the scattering density of the object, in other words, by the image of the object in reciprocal space. Since the Fourier image of a crystal is also a lattice, the crystal is represented in reciprocal space by the so-called *reciprocal lattice*. Each diffraction reflection corresponds to a specific node of the reciprocal lattice of the crystal, which is currently intersected by the so-called Ewald sphere - the set of possible wave vectors of the electron after elastic scattering (Figure 1.11). In this case, an amorphous body in reciprocal space represents a certain diffuse density distribution, and diffraction patterns from amorphous materials are diffuse halos.

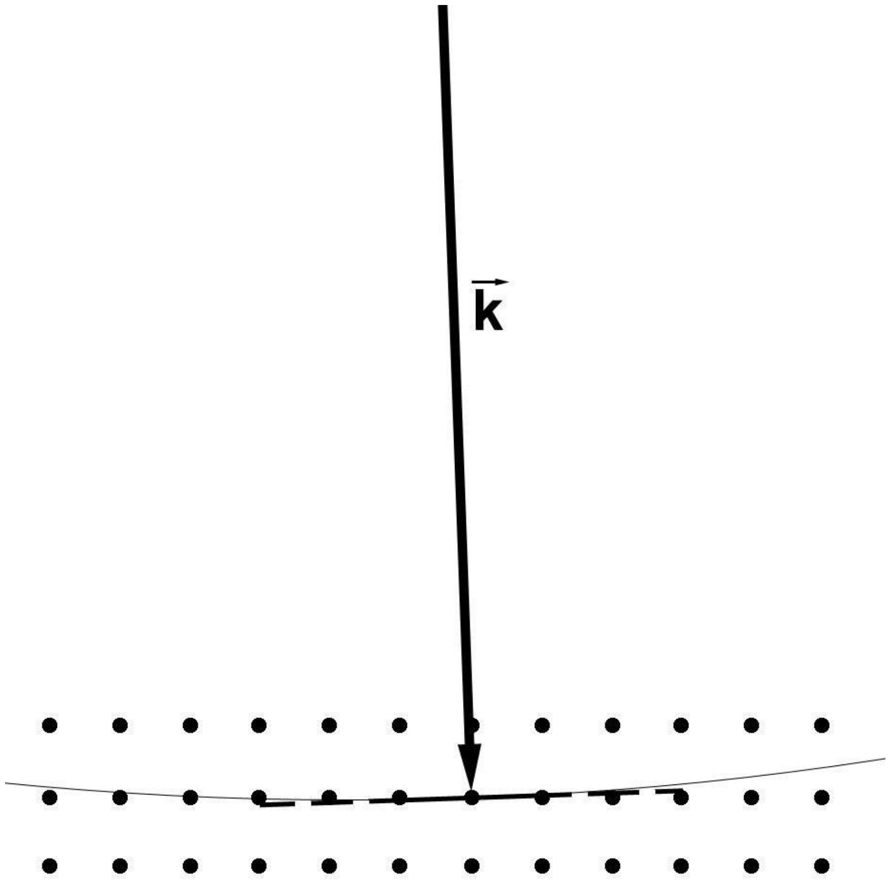


Figure 1.11 – Ewald’s sphere crossing the reciprocal lattice.

The type of diffraction pattern, in particular, the presence or absence of certain diffraction reflections, strongly depends on the relative orientation of the reciprocal grating relative to the incident electron beam. In addition, the integrated intensity of diffraction reflections, that is, the intensity of scattered electrons, varies greatly when the crystal is tilted, which differs significantly from the case of amorphous structures. For this reason, differently oriented crystallites will have different contrasts in TEM images even with the same elemental composition. This is called the phenomenon of *diffraction contrast*, a characteristic feature of crystalline materials (Figure 1.12).

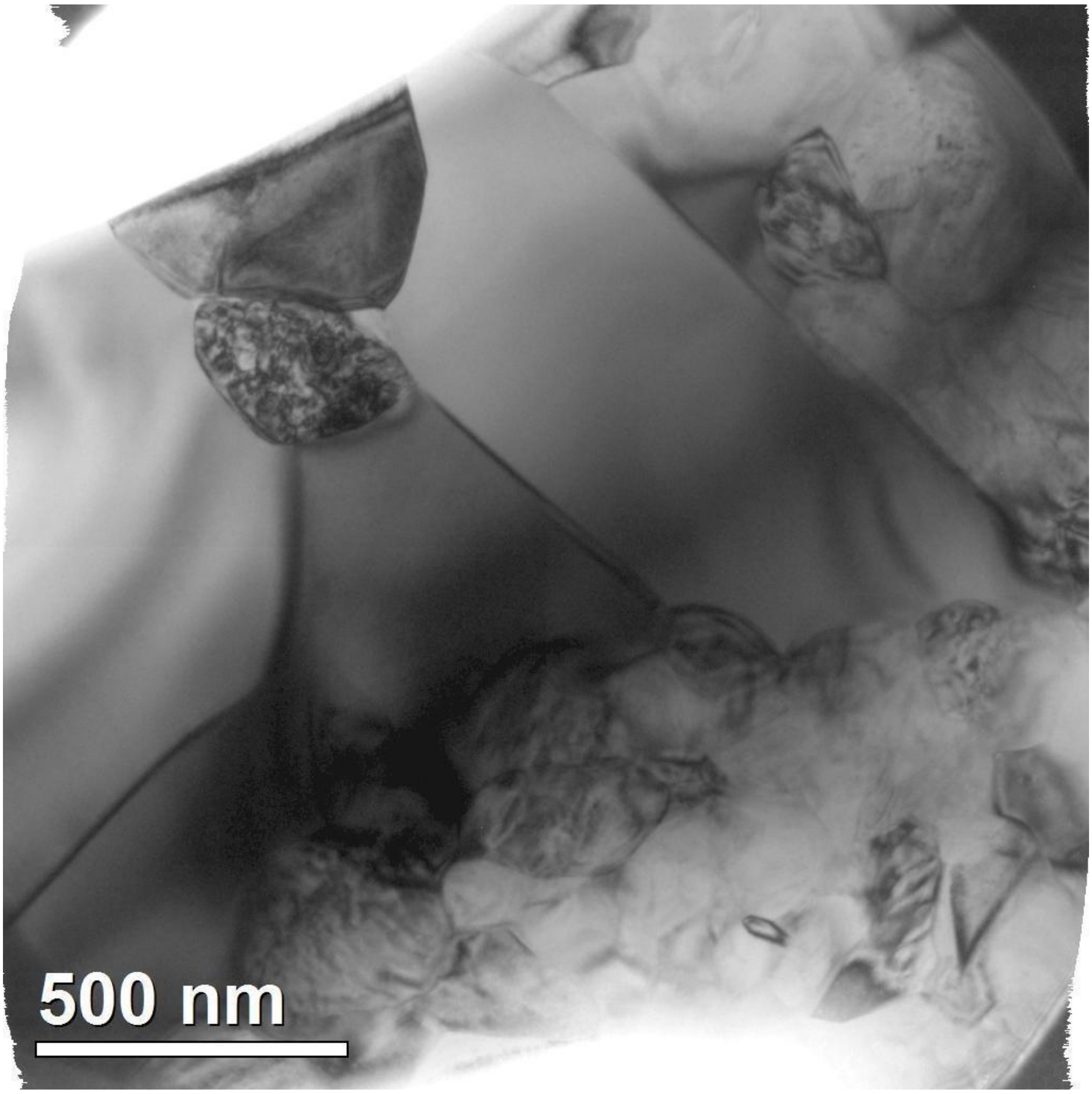


Figure 1.12 – Diffraction contrast in a polycrystalline material.

To enhance the contrast, you can use a special aperture located in the focal plane of the objective lens, where, in fact, the diffraction pattern is formed, the so-called *objective aperture*, in such a way as to cut off all diffracted electrons except one beam. If you leave only the transmitted beam, that is, unscattered electrons, then the contrast in the image will be determined by the integral scattering intensity of each section - the greater the scattering intensity, the darker the given crystallite. For example, if the incident beam is parallel to the atomic rows of a crystallite and, accordingly, perpendicular to the plane of its reciprocal lattice, then the diffraction intensity will be high, and the crystallite in the image will be the darkest. In this case, the absence of material in the electron path does not lead to any scattering, so such areas in the image will be as bright as possible. Images obtained when a transmitted beam/unscattered electrons enter an aperture, in which the empty field appears bright, are called *bright-field*.

Likewise, if the aperture is set so that it leaves only some of the scattered electrons, absorbing all the unscattered ones, such an image is called *dark-field*. Dark-field images show the holes in the sample to be completely black, since the vacuum does not dissipate anything. In this case, only those areas of the sample that scatter electrons in the direction in which the objective aperture is currently installed will be visible in such an image. For example, if you select a certain diffraction reflection in a diffraction pattern, then only those areas of the sample in which the structure creates this diffraction reflection will be visible in the dark-field image (Figure 1.13).

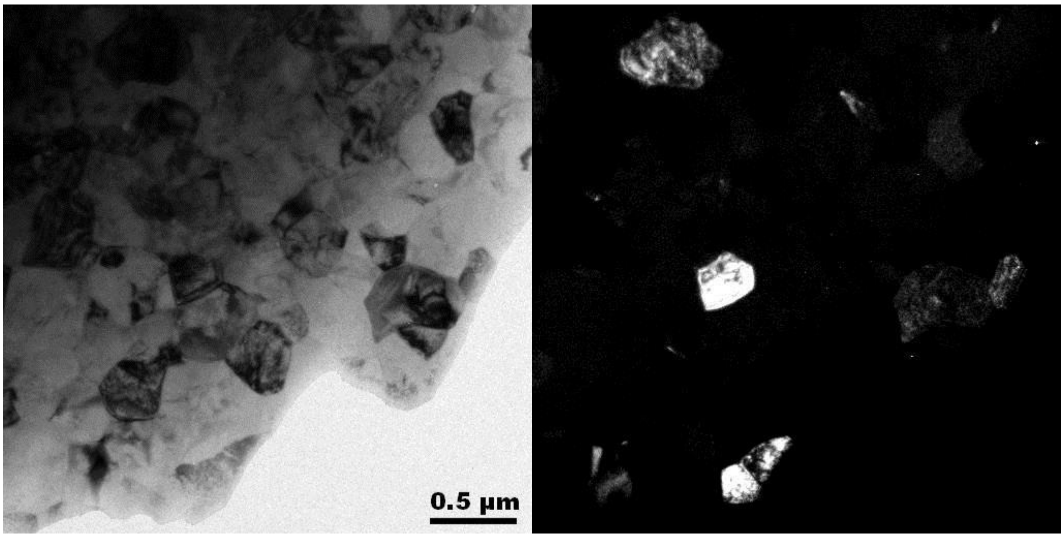


Figure 1.13 – Bright-field and dark-field images.

The use of diffraction contrast is a very powerful tool for the phase analysis of materials. In addition, diffraction contrast is one of the main sources of information about the crystallographic characteristics of extended defects in crystals (Figure 1.14).

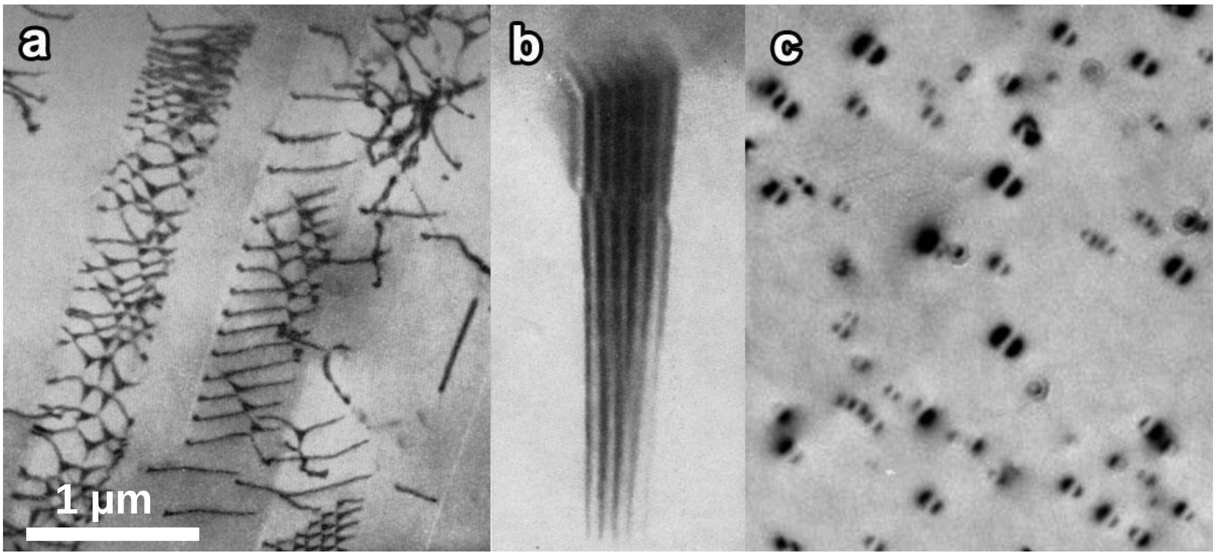


Figure 1.14 – Images of dislocations (a), stacking fault (b), inclusions (c).

The high resolution of TEM allows direct observation of the crystalline structure of materials, while the objective aperture must transmit at least 2-3 diffraction reflections (Figure 1.15).

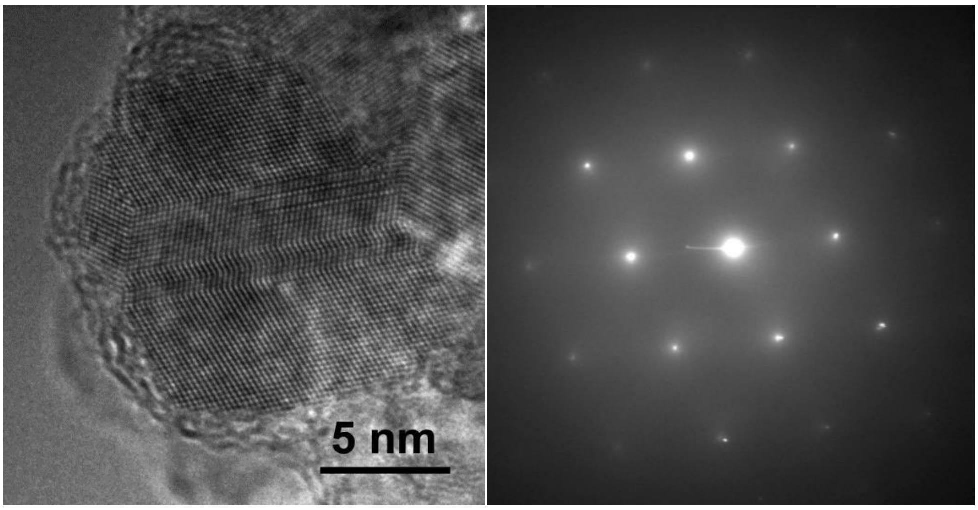


Figure 1.15 – High-resolution TEM image (HRTEM) of a diamond nanoparticle and the corresponding electron diffraction pattern.

HRTEM images make it possible to identify inclusions of another phase even less than a nanometer in size, the presence of some defects in the crystal structure and other structural features of materials almost at the atomic level (Figure 1.16).

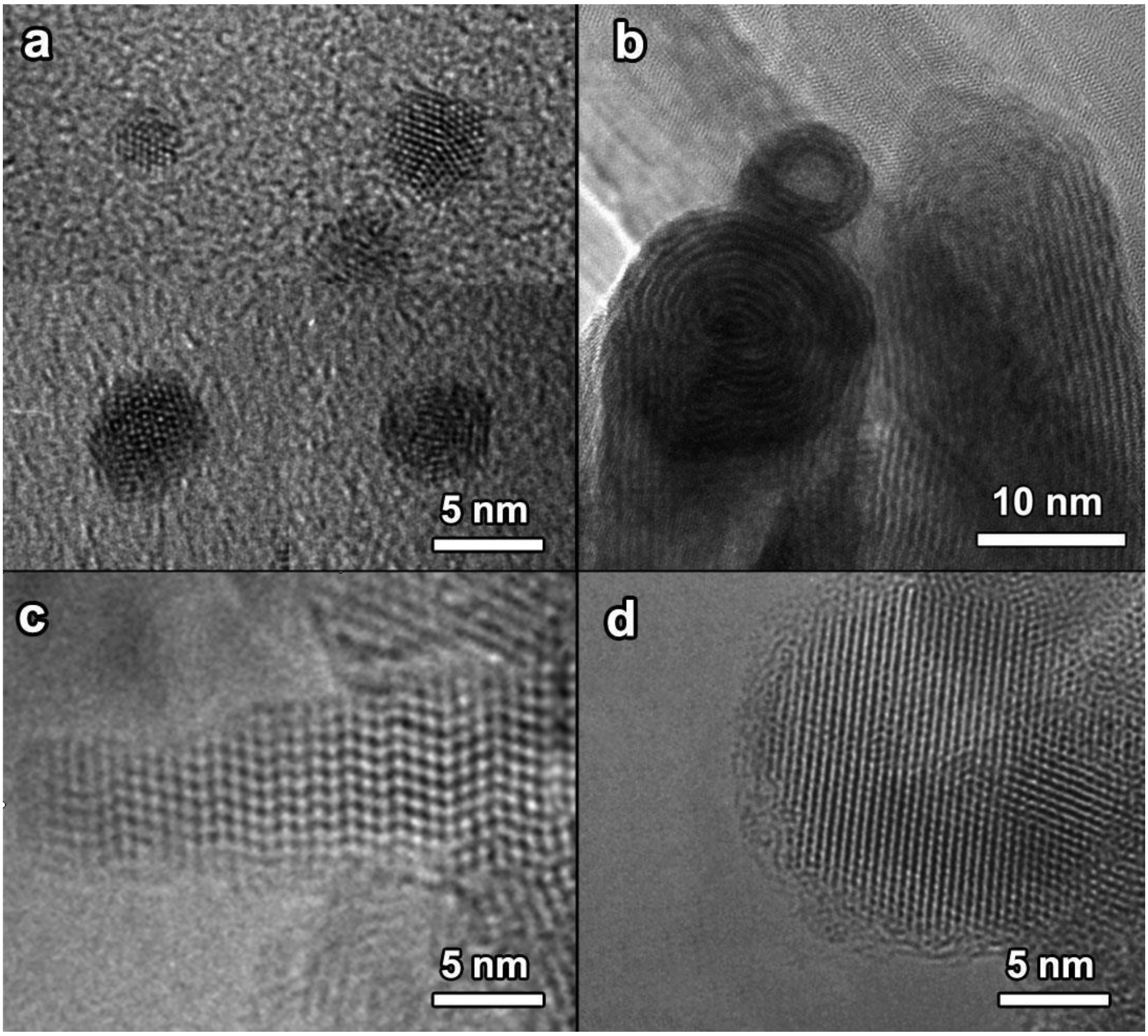


Figure 1.16 – HRTEM images of gold nanoparticles (a), inorganic nanotubes (b), whisker-like zinc sulfide nanocrystal (c), and lead fluoride nanoparticles (d).

Self-control questions:

1. What is the electron wavelength at 200 keV energy?

2. What is the lateral resolution of modern TEMs?
3. What is the difference between electron diffraction on amorphous and crystalline materials?
4. What is the essence of bright-field and dark-field technique?
5. How many diffracted beams are left by an objective aperture for diffraction contrast and for high-resolution imaging?

3. Scanning electron microscopy

Obtaining images with a relatively high resolution due to the short wavelength of electrons is also possible in another geometry, similar not to a biological microscope but to a metallographic one, that is, when recording electrons not passing through the sample but reflected. This allows, with a higher resolution than optical microscopes, to analyze nanodetails of the shape of objects too large to be transparent to fast electrons, that is, larger than a micrometer in size, or located on substrates of ordinary thickness, which can be many orders of magnitude greater than that required for TEM scale (≈100 nm).

The most widespread is the so-called “raster” method of obtaining such images, based on registration of reflected electrons. The essence of this approach is that an electron beam is focused on a sample into a spot of the smallest possible size (modern electron optics makes it possible to obtain <1 Å) and then the beam is scanned along a rectangular array of points (raster) on the surface. The image on the screen corresponds in its geometry to the scanning raster, but the intensity at each point of the image corresponds to the intensity of any recorded signal, for example, the flow of reflected electrons that occurs when the beam hits the corresponding point on the surface. This type of electron microscopy is called *scanning electron microscopy* (SEM).

This scanning approach has an important advantage compared to illuminating the sample with a wide beam and projecting the entire corresponding image onto the screen - when scanning at each moment of time, all signals resulting from the interaction of fast electrons with the sample relate to one specific point (Figure 2.1). This significantly expands the various analytical capabilities of this method, which will be discussed in more details below.

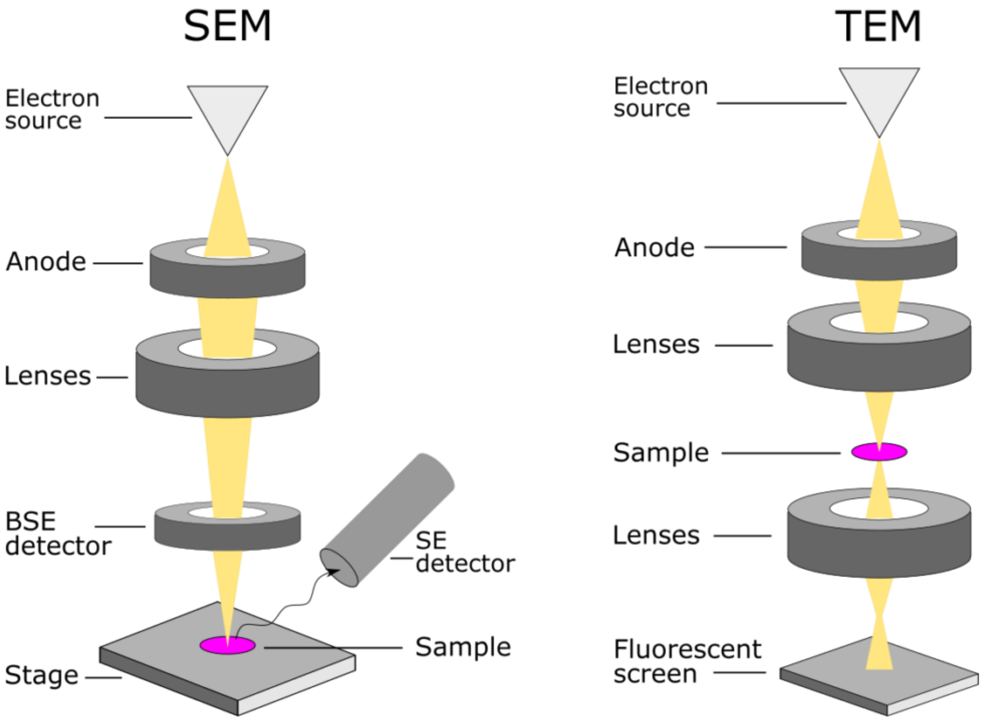


Figure 2.1 – Schematic diagrams for the implementation of SEM and TEM (AnaPath Research: [web-site]. URL: https://anapath.ch/electron-microscopy-2/).

For example, it is possible to record high-energy back-scattered electrons (BSE) or low-energy secondary electrons (SE) arising from the interaction of a point beam with a sample. The images obtained in this way in back-reflected and secondary electrons carry different information. The contrast in a BSE image is determined mainly by the density of the material, and objects even at some depth below the surface can be seen in the image. In the SE image, the contrast is determined by local electronic characteristics, that is, not only by the serial number of the elements, but also by the work function. In this case, secondary electrons appearing only in a thin surface layer are recorded, and thus, in fact, only a thin surface layer is visible in the image. However, in this case the lateral resolution of the method is much higher due to the reduced blurring effect due to electron scattering in the substance.

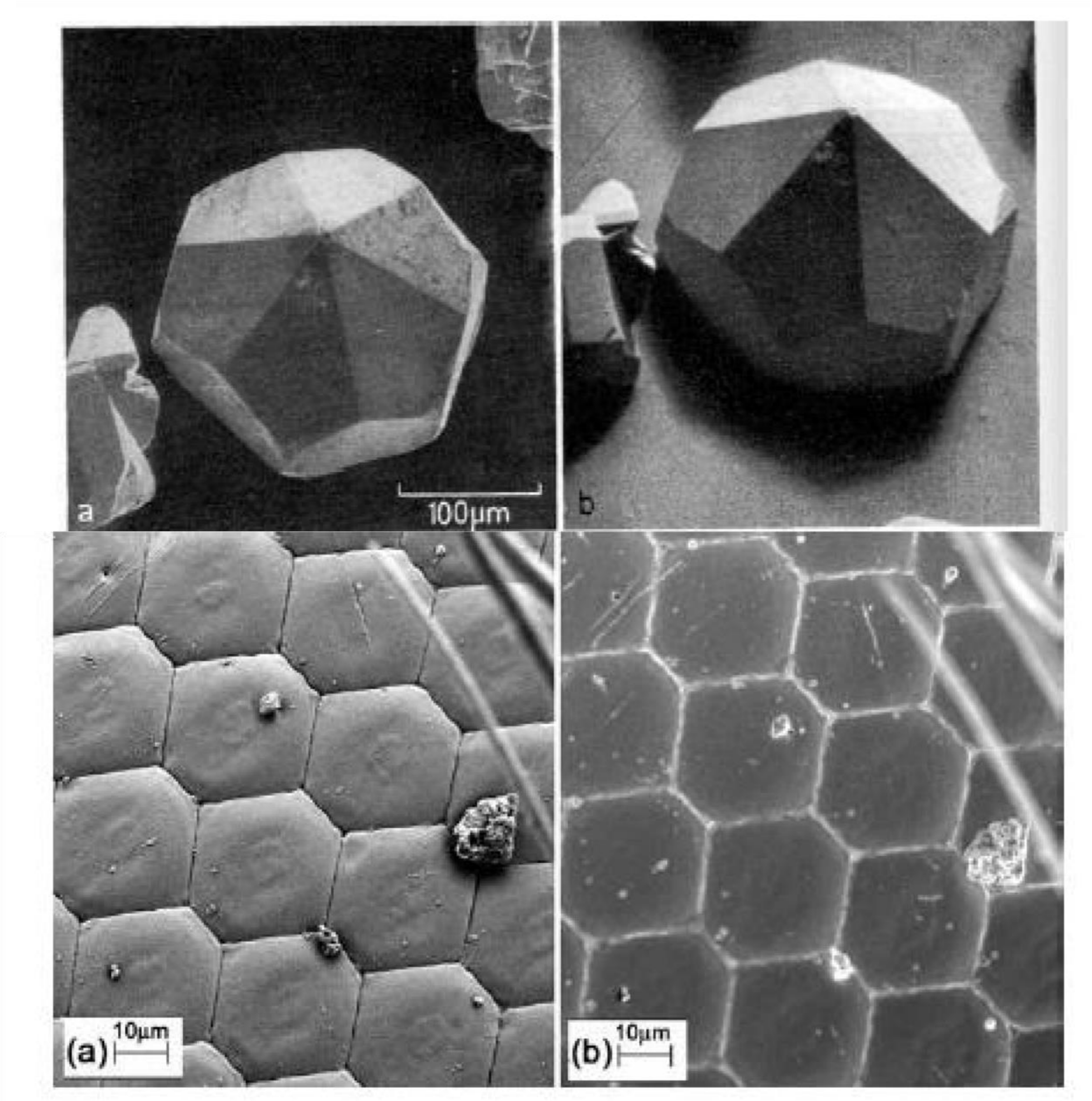


Figure 2.2 – Difference between images in secondary (SE) and back-reflected (BRE) electrons (Egerton R. F. Physical Principles of Electron Microscopy. Springer. 2005).

The reflection of electrons from crystalline materials depends on the angle of incidence; this fact allows to determine the crystallographic orientation of the grains of polycrystalline materials (Figure 2.3).

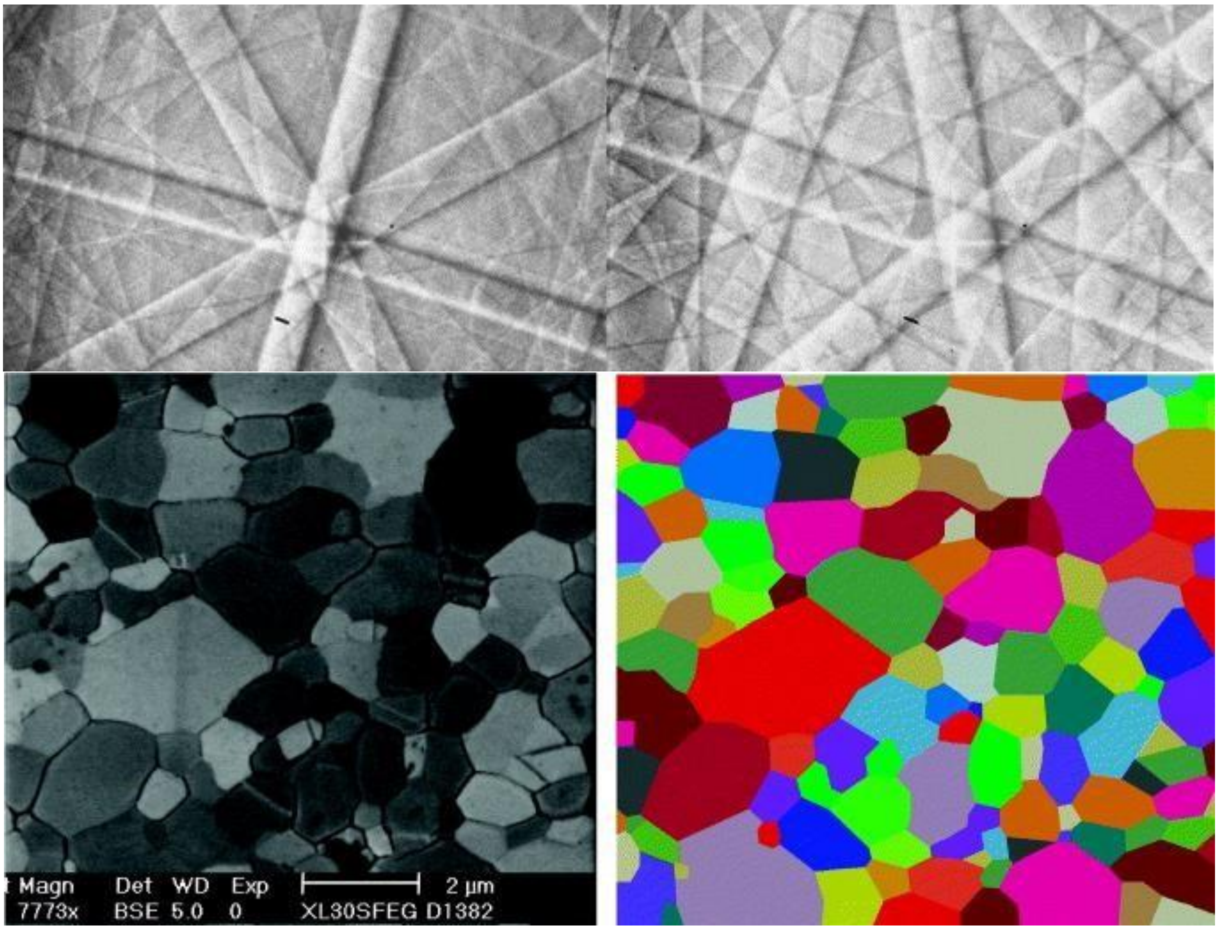


Figure 2.3 – SEM rocking patterns on crystalline surfaces and a map of crystallographic grain orientations.

In addition, it is also possible to obtain images by recording other signals arising from the interaction of fast electrons with matter. A number of analytical methods discussed in the next section are based on this and similar principles.

Self-control questions:

1. What does SEM stand for?

2. What is the fundamental difference between SEM and TEM?
3. Which technique provides the best resolution: SE or BSE?
4. How deep can we look inside the material using BSE?
5. What is topographic contrast?

4. Analytical methods

When high-energy particles interact with matter, electrons of atoms are knocked out, not only from the outer but also from the inner electron shells. If the knockout is carried out by an electron, then it will lose energy no less than the ionization potential of the corresponding shell; if by a photon, then it will be absorbed.

The energy of the innermost, the so-called K-shell, can be easily estimated using the formula for the energy of the ground state of a hydrogen-like atom:

$$E_i = Ry \times Z^2 \tag{3.1}$$

Where Ry is the Rydberg constant $\frac{4\pi^2 me^4}{h^2} = 13.6\ eV$, and Z is the nuclear charge in units of elementary charge, that is, the ordinal number of an element in the periodic table. Thus, the ionization potential of a hydrogen atom is only 13.6 eV, and if we replace its nucleus with a uranium nucleus with Z = 92, it will be more than 100,000 eV. This huge energy dispersion between elements is an important feature on which many of the analytical methods we will consider are based. It is important to emphasize that all these methods require the use of particles of sufficiently high energy.

Obviously, in atoms, excluding the hydrogen atom, there are many electrons that influence each other, but the more external electrons have only a weak screening effect on the internal ones and formula (3.1) is a good approximation, confirmed experimentally. Moreover, the emerging chemical bonds of elements, that is, a change in the state of the outer electrons, has little effect on the energies of the electrons of the inner shells, which are thus characteristic for the elements.

When an electron is knocked out from one of the inner shells, for example, by a high-energy electron, some other electron of the atom can move to the vacated orbital. In this case, the atom will emit a photon, and the energy of this photon will be very high; this radiation in the vast majority of cases will be called *characteristic X-ray radiation* and will lie in *the X-ray* part of the spectrum. Lines of this spectrum related to transitions to the K-shell are called K-series. Transitions from the next shell, i.e. L in this case, will give a K_{α} line from the second shell, i.e. M – K_{β}, etc. When taking into account the sublevels of data in the shell, the line designations acquire numerical indices - $K_{\alpha 1}$, $K_{\alpha 2}$, $L_{\beta 1}$, $M_{\alpha 1}$, $M_{\gamma 3}$, etc. (Figure 3.1)

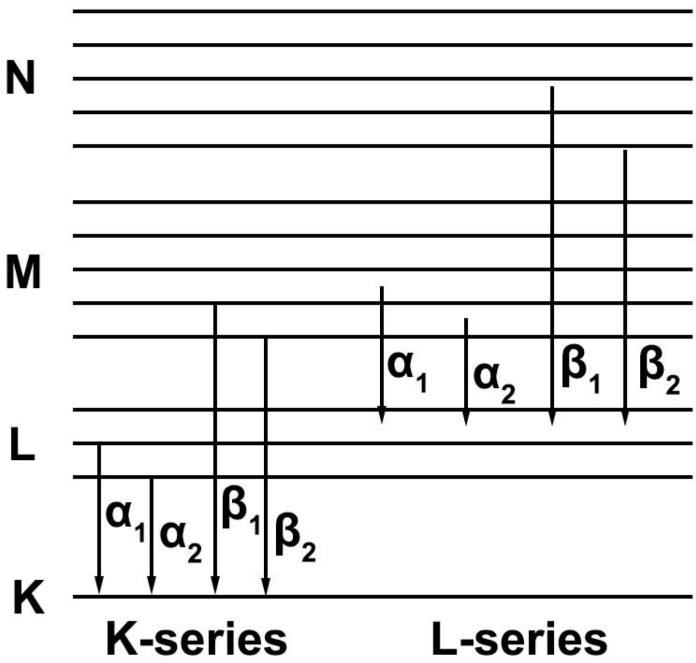


Figure 3.1 – Confirmation of the quadratic dependence of the energy of characteristic X-ray quanta on the ordinal number of elements.

The names of the shells are determined by the following. At first, the corresponding series were designated A, B, etc. But when the hypothesis arose that characteristic X-ray radiation is essentially the luminescence of atoms in the case of ionization of deep shells with a high ionization potential, there was no confidence that the ionization of the deepest, first, shells in the materials studied was achieved in the experimental setups. For this reason, for the highest energy series observed, the letter K was proposed from the middle of the alphabet in case lines of higher energy were subsequently discovered to reserve J, I, H, etc. for them. However, for the classical metals studied at that time, copper, aluminum, iron, the accelerating voltages in X-ray tubes were sufficient to ionize the first shells and spare letters were not required.

Measurements of the energy of the K and L series lines by Henry Moseley in 1914 showed excellent consistency with their dependence on the ordinal number of the element (Figure 3.3).

It is especially important that the characteristic energies of the L series are approximately an order of magnitude lower than the energies of the K series. The energies is M series, N series, etc. are even less. In particular, if the K series of copper is about 10 keV, then the L series is about 1 keV (Figure 3.2). Moreover, the number of series, naturally, does not exceed the line number of the periodic table in which the element is located. The energy spread between different elements and series can be assessed using the following scheme (Figure 3.4). By observing the spectrum of characteristic radiation, we can determine what elements our matter consists of, with the exception of hydrogen and helium.

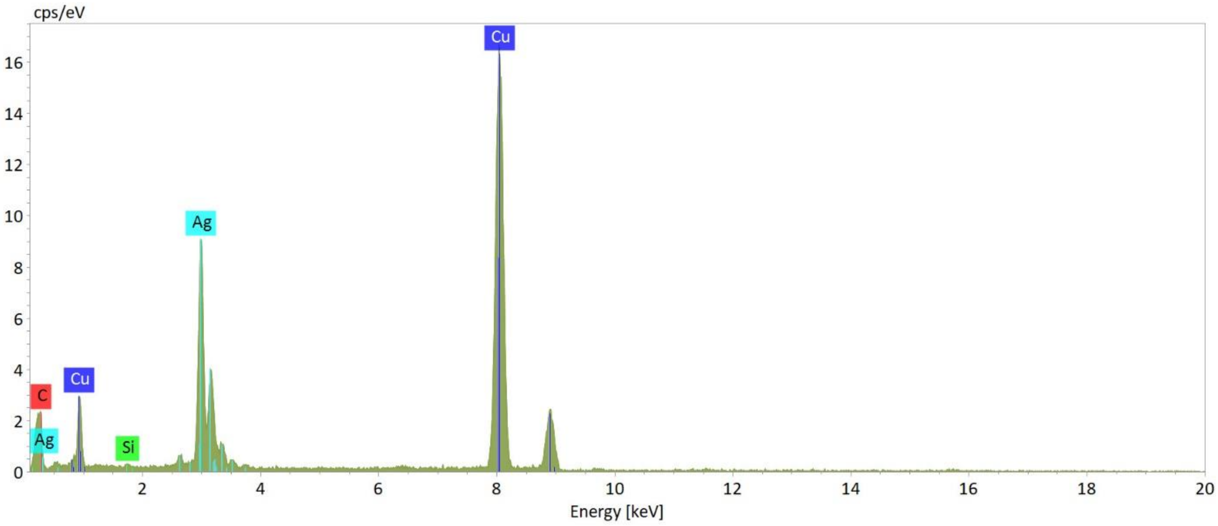
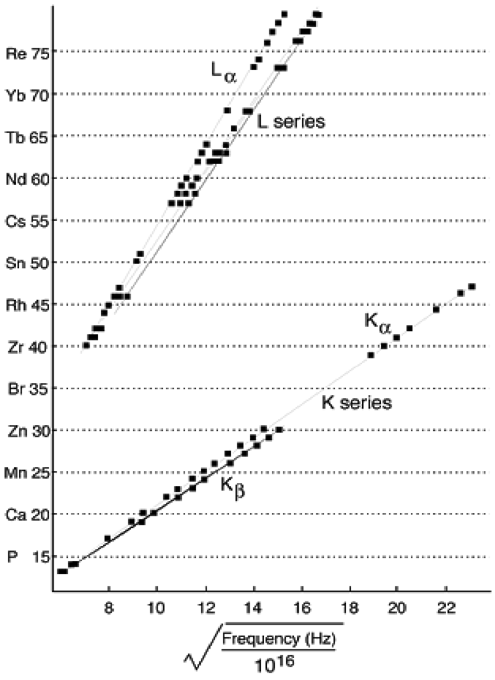


Figure 3.2 – Spectrum of characteristic x-ray radiation of copper/silver alloy.



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

Figure 3.3 – Confirmation of the quadratic dependence of the energy of quanta of characteristic X-ray radiation on the ordinal number of elements.

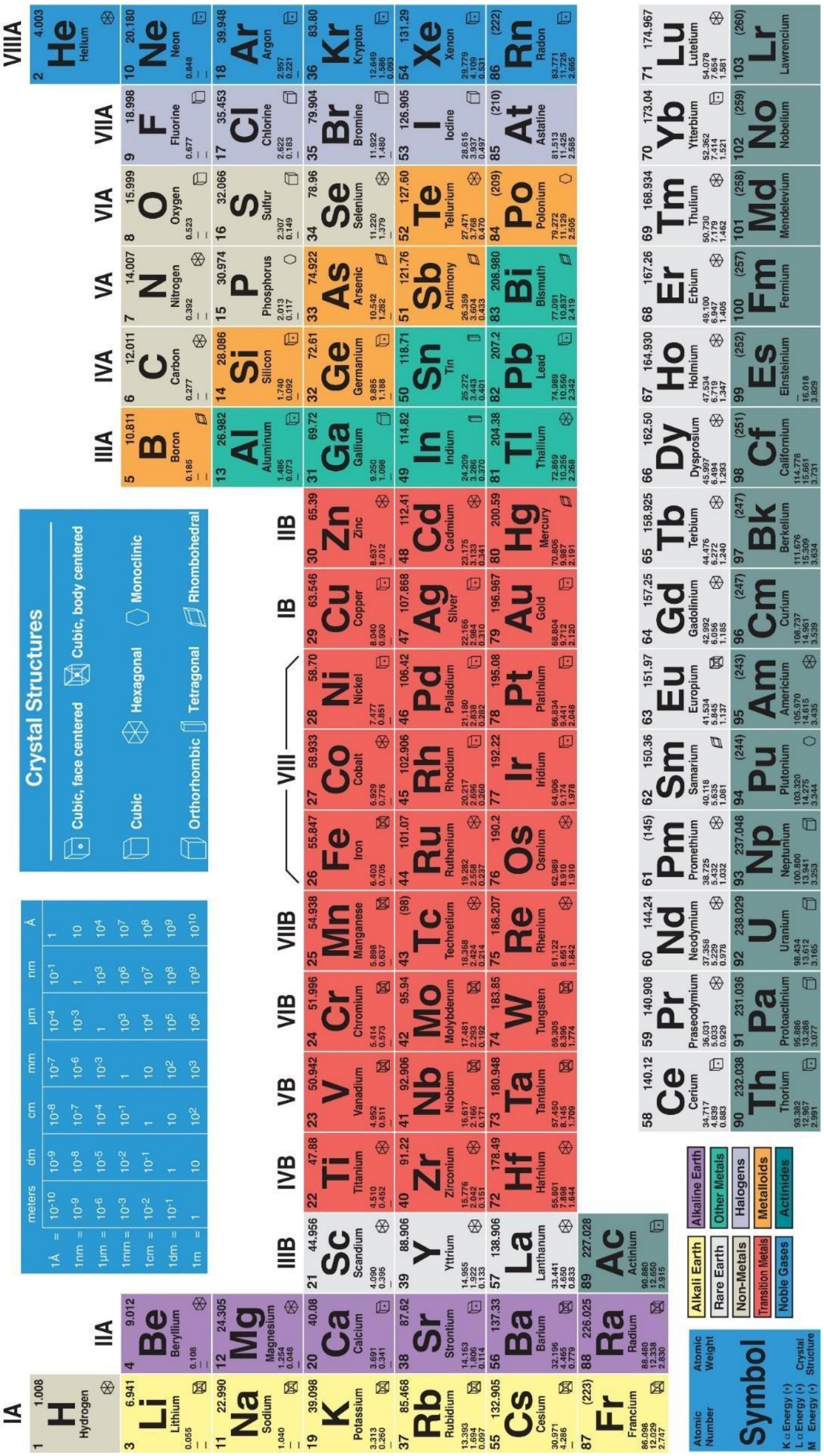


Figure 3.4 – Table of energies of the first lines of series of characteristic X-ray radiation (Ametek: [web-site], URL: https://www.edax.com/).

The following two methods are based on recording characteristic X-ray radiation: X-ray fluorescence analysis and X-ray spectral microanalysis. They differ only in the type of high-energy radiation used to excite characteristic X-rays. In the first case, short-wave X-ray radiation is used; in the second case, a high-energy electron beam is used. This difference determines the fundamental technical features of each method.

X-ray radiation is a penetrating radiation and is relatively weakly absorbed by air. X-ray fluorescence analysis makes it possible to determine the composition even in the field; however, the lack of effective X-ray optics does not allow this method to have high spatial resolution.

In the case of X-ray spectral microanalysis, the excitation source is an electron beam. This immediately determines two important features: firstly, to use this method, a vacuum chamber is required in which the material under study is placed, that is, serious restrictions appear on the dimensions, state of aggregation, etc.; secondly, the electron beam can be focused in a very small spot, thus, this method can have a relatively high resolution, which is why it is called “microanalysis”.

Both methods allow to determine the elemental composition from the recorded spectra (Figure 3.5), since the position of the peaks is characteristic of each element. In addition, the quantitative composition can be determined from the intensities of the spectrum lines.

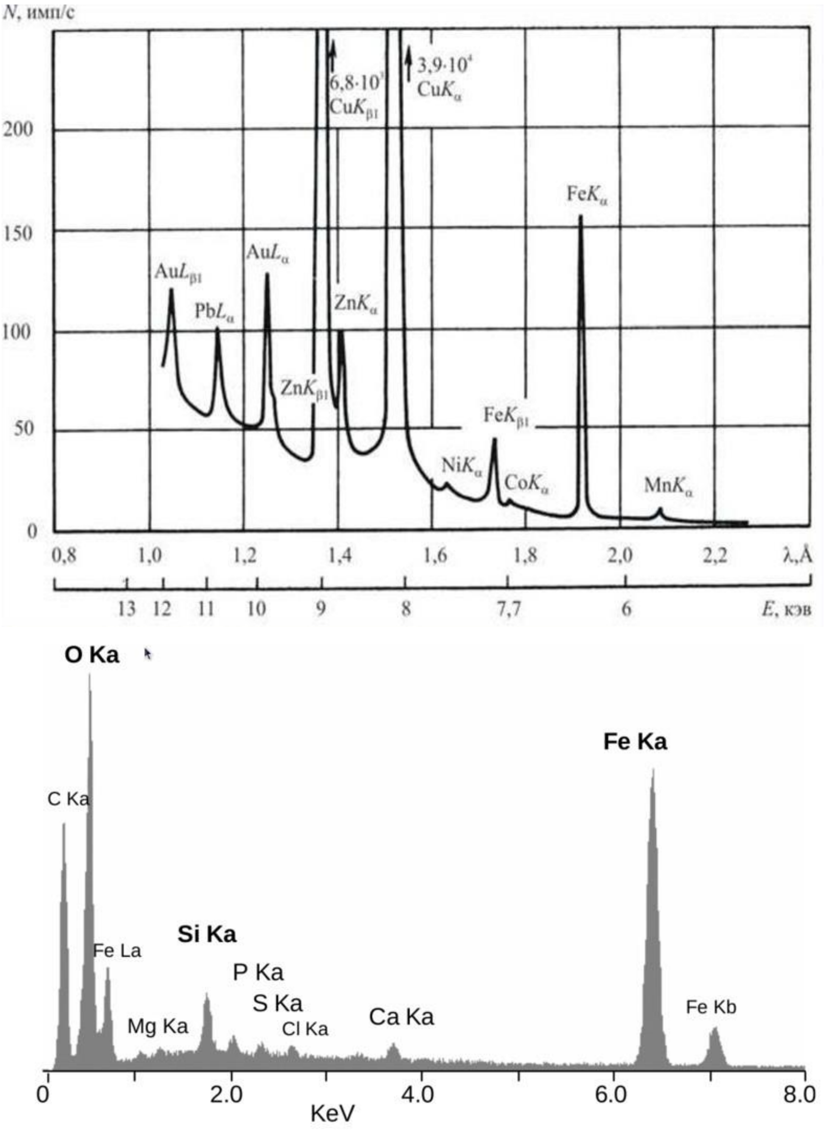


Figure 3.5 – Examples of characteristic X-ray radiation spectra obtained using the methods of X-ray fluorescence analysis and X-ray spectral microanalysis (Рентгеновские методы спектрального анализа [Electronic source]. URL:https://en.ppt-online.org/727161).

The resolution of X-ray spectral microanalysis is determined by the physics of the interaction of a beam of fast electrons with matter, mainly by the size of the region where characteristic X-ray radiation is generated (Figure 3.6).

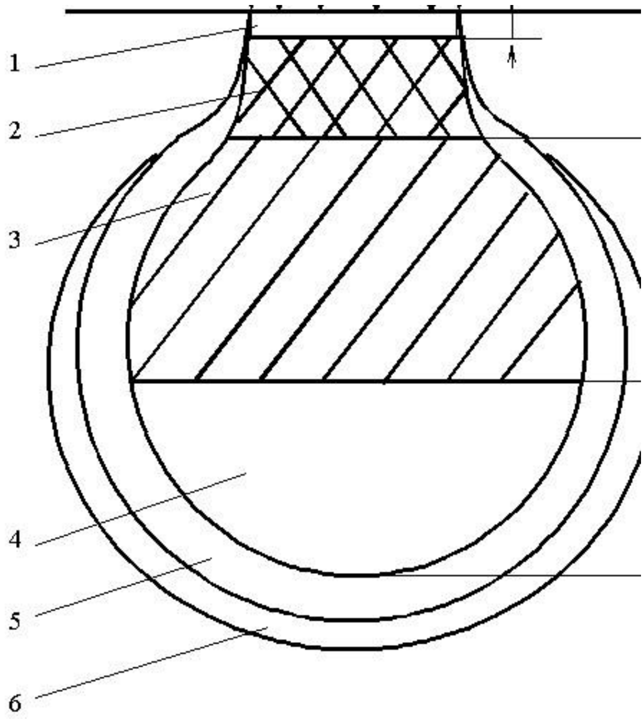


Figure 3.6 – Geometry of interaction of fast electrons with matter. 1 – region of Auger electron output, 2 – region of secondary electron output, 3 – region of back-reflected electron output, 4 – region of characteristic X-ray generation, 5 – region of bremsstrahlung X-ray generation, 6 – fluorescence generation region.

It is important to take into account that the size of the region where characteristic X-ray radiation is generated depends not only on the density of the material, but also on the energy of the electrons (Figure 3.7).

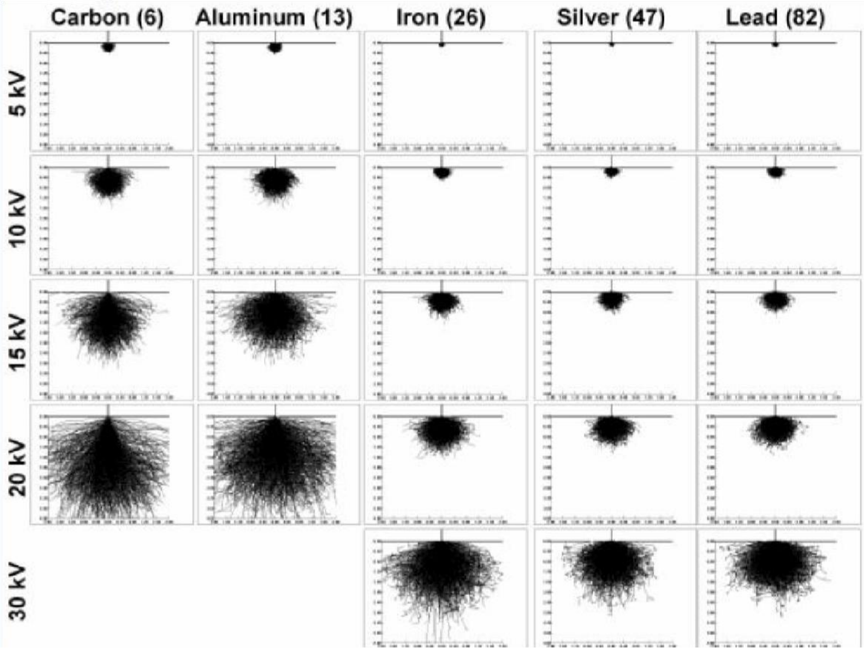


Figure 3.7 – Results of modeling the scattering of fast electrons in matter depending on the material and electron energy (Electron beam-specimen interaction [Electronic source]. URL: http://bbcc.unile.it/c/document_library/get_file?folderId=3021404&name=DLFE-200726.pdf).

The resolution of X-ray microanalysis is thus 100 nm – 1 μm, depending on the experimental parameters mentioned.

The resolution of the method can be increased by applying it to thin samples, such as those used in TEM, then there is no volume of material sufficient for extensive scattering and the resolution approaches the diameter of the electron beam, which can reach small fractions of a nanometer. Thus, the resolution of a method can significantly depend on the specific scheme of its implementation.

A characteristic feature of these methods, based on recording characteristic X-ray radiation, is the relatively low energy resolution of the spectra due to the difficulties of recording the so-called "penetrating radiation", and also due to the fact that spontaneous radiation is emitted evenly in all directions. Next, we will consider methods that allow us to extract more information about the structure of matter.

Self-control questions:

1. What is the energy for K-series lines for C (carbon) and Cu (copper)?
2. What is the lateral resolution of the analytical techniques?
3. How big is the difference in the energies of the K-series and L-series?
4. How large is the penetration depth of high-energy electrons in carbon and iron?
5. Why do we have to use high-energy electrons?

5. Electron energy loss spectroscopy

Electron energy loss spectroscopy (EELS) is a measurement of the energy spectrum of electrons from a primary beam passing through a sample. The energy resolution of measuring such spectra can reach fractions of an electronvolt, which makes it possible not only to determine the elemental composition, but also to characterize the chemical bond in which each element is located.

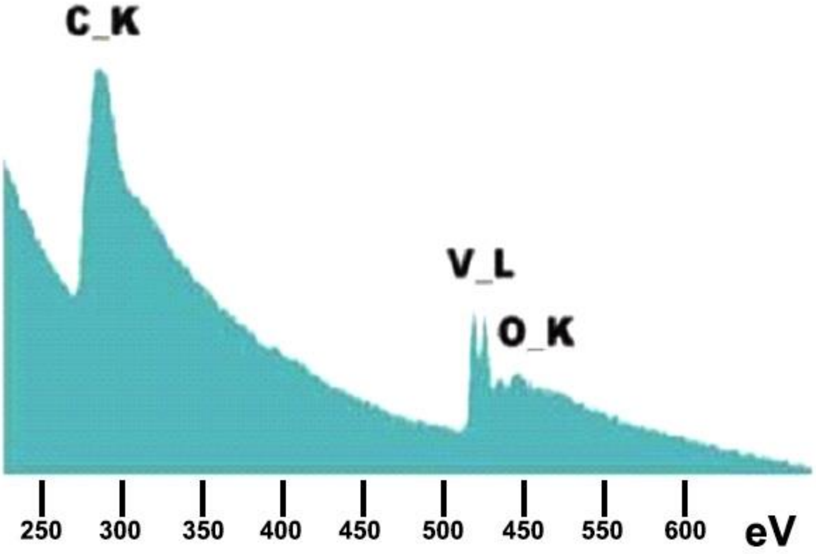


Figure 4.1 – Typical EELS spectrum, edges marked losses of carbon, vanadium and oxygen.

With an increase in valence, the degree of screening by electrons of the field of the atomic nucleus decreases and the binding energies of all remaining electrons increase, which is manifested at probing the inner electron shells (Figure 4.2). This effect is called *chemical shift* . By measuring its value, you can evaluate the type of chemical bond of an element and measure its valency.

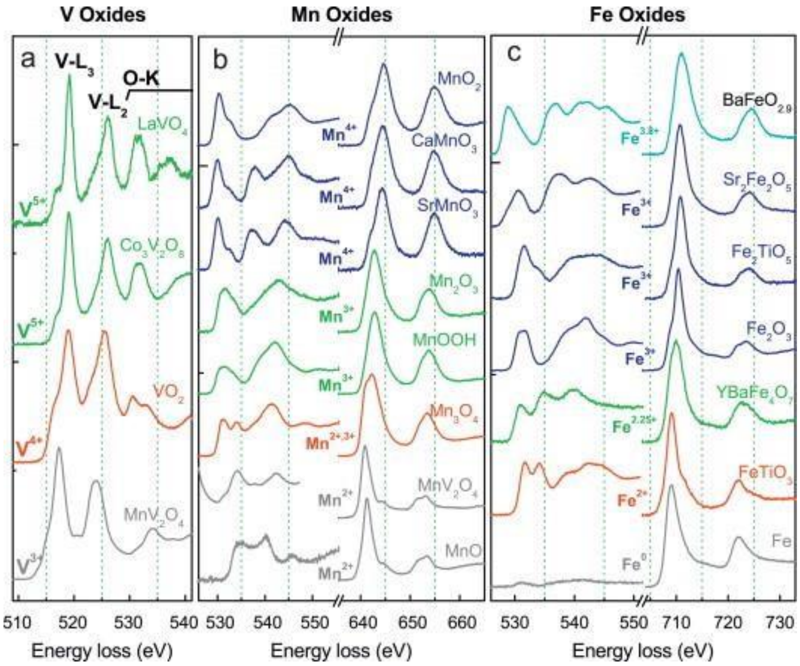


Figure 4.2 – Edges of loss of various metals and oxygen in various compounds (Tan H., Verbeeck J., Abakumov A., Van Tendeloo G. Oxidation state and chemical shift investigation in transition metal oxides by EELS // Ultramicroscopy. – 2012. – V. 116. – P. 24-33).

The peculiarity of using EELS is that since an electron beam is used as the primary beam, it is possible to obtain this analytical information from areas of extremely small volume; the resolution of this method is a fraction of a nanometer when used in TEM. However, this assumes relatively high electron energy, which makes it somewhat difficult to accurately measure small variations in their energy. In addition, the resolution-limiting factor, as always in electron microscopy, is the stability of the material under study under the electron beam.

Self-control questions:

1. What is the characteristic energy resolution of EELS?
2. Can we use EELS for the chemical composition determination?
3. Can we detect the chemical shift by EELS?
4. What lateral resolution can we achieve with EELS?
5. How can we measure a valence state of an element by EELS?

6. X-ray photoelectron spectroscopy

Registration of secondary electrons arising under the influence of monochromatic X-ray radiation also makes it possible to obtain information about the binding energies of electrons in the substance under study (Figure 5.1).

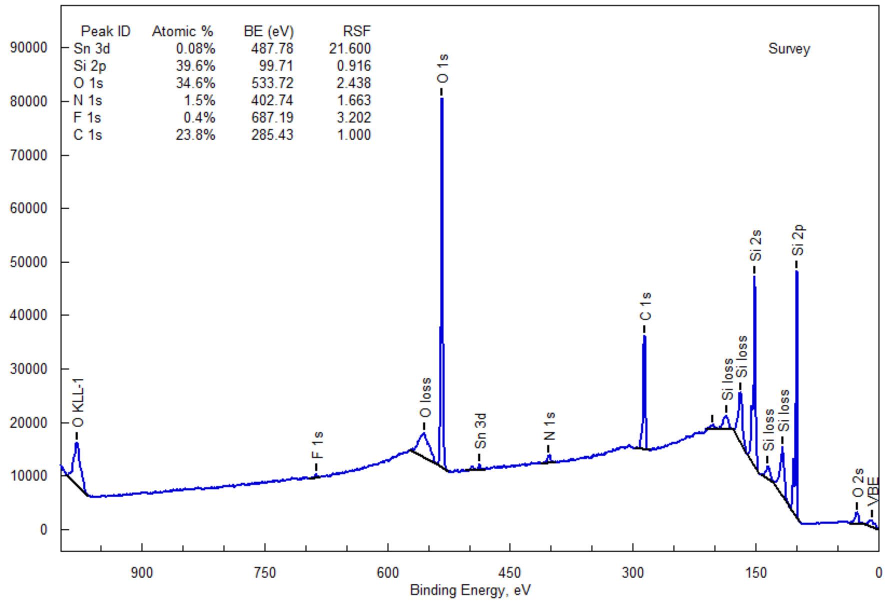


Figure 5.1 – Typical X-ray photoelectron spectrum (The XPS library: [web-site]. URL: https://xpslibrary.com/spectra-data-processor-sdp/).

The advantage of this approach is that it allows registering secondary electrons with energies of the order of tens of hundreds of electron volts. Thus, higher accuracy in measuring their energy is available. However, the use of X-ray radiation in the primary beam suggests that this method does not have high locality. At the same time, X-ray photoelectron spectroscopy is one of the most widely used techniques for analyzing the structure of new materials, particularly due to its high precision in chemical shift measurements.

Self-control questions:

1. What does XPS stand for?
2. What is the main advantage of XPS?
3. Does it provide specifically different from EELS information?
4. What is the lateral resolution of XPS?
5. How will a specimen charging influence XPS measurements?

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DIRECT TECHNIQUES OF STRUCTURE INVESTIGATION

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