Transmission Electron Microscopy

A Textbook for Materials Science

Transmission Electron Microscopy

I Basics

The Transmission Electron Microscope

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CHAPTER PREVIEW

A typical commercial transmission electron microscope (TEM) costs about $2 for each electron volt of energy in the beam, and if you add on all the options, it can cost about $4–5 per eV. As you'll see, we use beam energies in the range from 100,000–400,000 eV, so a TEM becomes an extremely expensive piece of equipment. Consequently, there have to be very sound scientific reasons for investing such a large amount of money in one microscope. In this chapter (which is just a brief overview of many of the concepts that we'll talk about in detail throughout the book) we start by introducing you to some of the historical development of the TEM because the history is intertwined with some of the reasons why you need to use a TEM to characterize materials. Other reasons for using TEM appeared as the instrument developed. Unfortunately, coupled with the advantages are some serious drawbacks, which limit the microscope performance, and you must be just as aware of the instrument's limitations as you are of its advantages, so we summarize these also.

A TEM can appear in several different forms, all of which are described by different acronyms such as HRTEM, STEM, and AEM, and we'll introduce you to these different instruments. We'll also use the same acronym to denote both the technique (microscopy) and the instrument (microscope). We regard all of the dif-

ferent types of TEM as simply variations on a basic theme and that is why only "TEM" is in the book title. We will describe some of the basic physical characteristics of the electron. Throughout the book you'll have to confront some physics and mathematics every now and again. The reason for this is because understanding what we can do with a TEM and why we operate it in certain ways is governed by the fundamental physics of electrons, how electrons are controlled by magnetic fields in the microscope, and how electrons interact with materials.

Finally, we will summarize some of the most popular computer software packages for TEM. We will refer to many of these throughout the text. We are including them in the first chapter to emphasize the role of the computer in today's TEM analysis.

The Transmission Electron Microscope

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1.1. WHY USE ELECTRONS?

Why should we use an electron microscope? Historically, TEMs were developed because of the limited image resolution in light microscopes, which is imposed by the wavelength of visible light. Only after electron microscopes were developed was it realized that there are many other equally sound reasons for using electrons, most of which are utilized to some extent in a modern TEM. By way of introduction to the topic let's look at how the TEM developed and the pros and cons of using such an instrument.

1.1.A. An Extremely Brief History

Louis de Broglie (1925) first theorized that the electron had wave-like characteristics, with a wavelength substantially less than visible light. Then Davisson and Germer (1927) and Thompson and Reid (1927) independently carried out their classic electron diffraction experiments which demonstrated the wave nature of electrons. It didn't take long for the idea of an electron microscope to be proposed, and the term was first used in the paper of Knoll and Ruska (1932). In this paper they developed the idea of electron lenses into a practical reality, and demonstrated electron images taken on the instrument shown in Figure 1.1. This was a most crucial step, for which Ruska received the Nobel Prize, somewhat late, in 1986. Within a year of Knoll and Ruska's publication, the resolution limit of the light microscope was surpassed. Ruska, surprisingly, revealed that he hadn't heard of de Broglie's ideas about electron waves and thought that the wavelength limit didn't apply to electrons. TEMs were developed by commercial companies only four years later. The Metropolitan-Vickers EM1 was the first commercial TEM. It was built in the UK in 1936, but apparently it didn't work very well and regular production was really started by Siemens and Halske in Germany in 1939. TEMs became widely available from several other sources (Hitachi, JEOL, Philips and RCA, *inter alia*) after the conclusion of World War II.

For materials scientists a most important development took place in the late 1940s when Heidenreich (1949) first thinned metal foils to electron transparency. This work was followed up by Bollman in Switzerland and Hirsch and co-workers in Cambridge. Because so much of the early TEM work examined metal specimens, the word "foil" has come to be synonymous with "specimen." In addition, the Cambridge group also developed the theory of electron diffraction contrast with which we can now identify, often in a quantitative manner, all known line and planar crystal defects in TEM images. This theoretical work is summarized in a formidable but essential text often referred to as the "Bible" of TEM (Hirsch *et al.* 1977). For the materials scientist, practical applications of the TEM for the solution of materials problems were pioneered in the United States by Thomas and first clearly expounded in his text (Thomas 1962). Other materials-oriented texts followed, e.g., Edington (1976) and Thomas and Goringe (1979).

Today, TEMs constitute arguably the most efficient and versatile tools for the characterization of materials. If you want to read a history of the TEM, the book by Marton (1968) is a compact, personal monograph and that edited by Hawkes (1985) contains a series of individual reminiscences. Fujita (1986) emphasizes the contribution of Japan to the development of the instrument. The field is now at the point where many of the pioneers have put their memoirs down on paper, or Festschrifts have been organized in their honor (e.g., Cosslett 1979, Ruska 1980, and Hashimoto 1986) which detail their contributions over the decades, and compile some useful overview papers of the field. If you enjoy reading about the history of science, we strongly recommend the review of *Fifty Years of Electron Diffraction,* edited by Goodman (1981), and *Fifty Years of X-ray Diffraction,* edited by Ewald (1962). (The spelling of X-ray is discussed in the *CBE Manual,* 1994.)

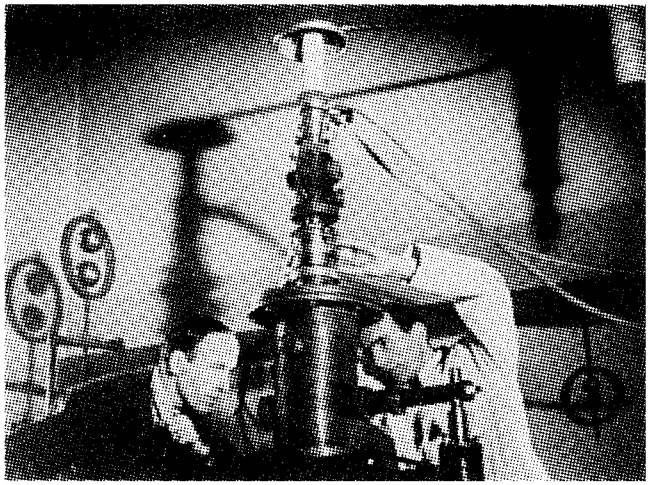


Figure 1.1. The electron microscope built by Ruska and Knoll in Berlin in the early 1930s.

1.1.B. Microscopy and the Concept of Resolution

When asked what a "microscope" is, most people would answer that it is an instrument for magnifying things too small to see with the naked eye, and most likely they would be referring to the visible-light microscope. Because of the general familiarity with the concept of the light microscope, we will draw analogies between electron and visible-light microscopes wherever it's instructive.

The smallest distance between two points that we can resolve with our eyes is about 0.1–0.2 mm, depending on how good our eyes are, and assuming that there's sufficient illumination to see by. This distance is the *resolution* or *resolving power* of our eyes. So any instrument that can show us pictures (or "images" as we'll refer to them) revealing detail finer than 0.1 mm could be described as a microscope, and its highest useful magnification is governed by its resolution. A major attraction to the early developers of the TEM was that, since electrons are smaller than atoms, it would be possible, at least theoretically, to build a microscope that could "see" detail well below the atomic level. The idea of being able to "see" with electrons may be confusing to you. Our eyes are not sensitive to electrons. If a beam of high-energy electrons was aimed into your eye, you would most likely be blinded as the electrons killed the retinal cells, but you wouldn't see anything! So an integral part of any electron microscope is a viewing screen of some form, which translates electron intensity to light intensity, and which we observe or record photographically. We'll discuss these screens and other ways of recording electron images in Chapter 7.

The resolution of a TEM means different things for different functions of the instrument, and we'll discuss them in the appropriate chapters. It's easiest to think of the image resolution in TEM in terms of the classical Rayleigh criterion for light microscopy, which states that the smallest distance that can be resolved, δ, is given approximately by

$$\delta = \frac{0.61\lambda}{\mu \sin \beta} \qquad [1.1]$$

In equation 1.1, λ is the wavelength of the radiation, μ the refractive index of the viewing medium, and β is the semi-angle of collection of the magnifying lens. For the sake of simplicity we can approximate $\mu \sin \beta$ (which is sometimes called the numerical aperture) to unity and so the resolution is equal to about half the wavelength of light. For green light in the middle of the visible spectrum, λ is about 550 nm (5500 Å), and so the resolution of a good light microscope is about 300 nm. In TEMs we can approximate the resolution in equation 1.1 to $0.61\lambda/\beta$ which, as we'll see later, is very small.

> We'll try to use nanometers throughout this book, but you'll find that many microscopists still insist on using Angstroms rather than the SI units. However, the Angstrom is close to the atomic diameter and so is a more convenient unit because it saves us using convoluted phrases like "three tenths of a nanometer."

Now although 300 nm is a small dimension to us it corresponds to about 1000 atom diameters, and therefore many of the features that control the properties of materials are on a scale well below the resolution of the light microscope. So there's a real need to image detail down to the atomic level if we want to understand the properties of materials, and that's a major reason why TEMs are so useful.

This limit of light microscopy was well understood at the turn of this century and prompted Ernst Abbe, one of the giants in the field, to complain that "it is poor comfort to hope that human ingenuity will find ways and means of overcoming this limit." (He was right to be so depressed because he died in 1905, some 20 years before de Broglie's ingenuity solved the problem.) Now de Broglie's famous equation shows that the wavelength of electrons is related to their energy, E, and if we ignore relativistic effects we can show approximately (and exactly in Section 1.4 below) that

$$\lambda \sim \frac{1.22}{E^{1/2}} \qquad [1.2]$$

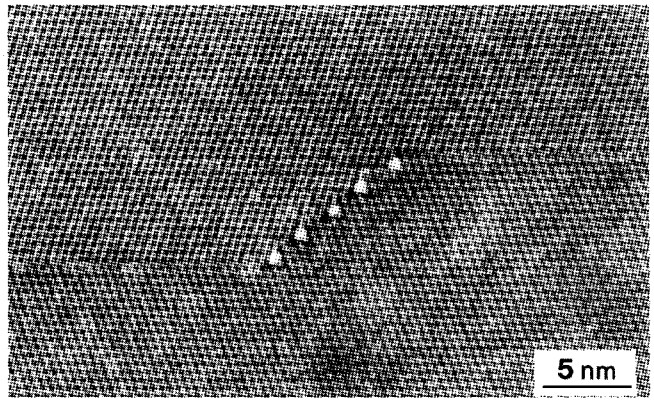


Figure 1.2. A twin boundary in spinel stepping from one {111} plane to another parallel plane. The white dots are columns of atoms. The change in atomic orientation across the twin boundary can be readily seen, even if we do not know what causes the white dots or why, indeed, they are white.

In this equation E is in electron volts (eV) and λ in nm. Remember that we should be precise in our use of the units V and eV: the former represents the *accelerating voltage* of the microscope while the latter refers to the *energy* of the electrons in the microscope. So for a 100-keV electron, we find that $\lambda \sim 4$ pm (0.004 nm), which is much smaller than the diameter of an atom.

We'll see later that we are nowhere near building TEMs that approach this wavelength limit of resolution, because we can't make perfect electron lenses (see Chapter 6). But progress was rapid after Ruska's early work on lenses and, since the mid-1970s, many commercial TEMs have been capable of resolving individual columns of atoms in crystals, creating the field of "high-resolution transmission electron microscopy," or HRTEM, which we'll discuss in Chapter 28. A typical HRTEM image is shown in Figure 1.2. The advantages of shorter wavelengths led in the 1960s to the development of high voltage electron microscopes (HVEMs), with accelerating potentials between 1 MV and 3 MV. In fact, most of these instruments were used to introduce controlled amounts of radiation damage into specimens in an attempt to simulate nuclear reactor environments, but changes in the emphasis of energy research mean there is not much call for such instruments today. While we can still improve the resolution by incremental amounts, the drive for much better resolution is now no longer paramount and the TEM is developing in other ways. In fact, only one HVEM (1 MV) for HRTEM imaging was constructed in the 1980s and three 1.25-MV machines in the 1990s. Intermediate voltage electron microscopes (IVEMs) were introduced in the 1980s. These TEMs operate at 300 or 400 kV, but still offer very high resolution, close to that achieved at 1 MV.

1.1.C. Interaction of Electrons with Matter

Electrons are one type of "ionizing radiation," which is the general term given to radiation that is capable of removing one of the tightly bound inner-shell electrons from the attractive field of the nucleus.

One of the advantages to using ionizing radiation is that it produces a wide range of secondary signals from the specimen, and some of these are summarized in Figure 1.3. Many of these signals are used in "analytical electron microscopy," or AEM, giving us chemical information and a lot of other detail about our samples. AEM uses X-ray energy dispersive spectrometry (XEDS) and electron energy-loss spectrometry (EELS). For example, Figure 1.4A is an X-ray spectrum from a very small region of a TEM specimen showing characteristic peaks which identify the elements present. We can transform such spectra into quantitative data describing elemental changes associated with inhomogeneous microstructures as also shown in Figures 1.4B and C. This aspect comprises Part IV of the book. In contrast, microscopes using nonionizing radiation such as visible light usually only generate light (but not much heat, which is good). AEMs generally offer improved performance at intermediate voltages, similar to HRTEMs.

In order to get the best signal out of our specimens we have to put the best signal in, and so the electron source is critical. We are now very accomplished in this respect as you'll see in Chapter 5, so modern TEMs are very good

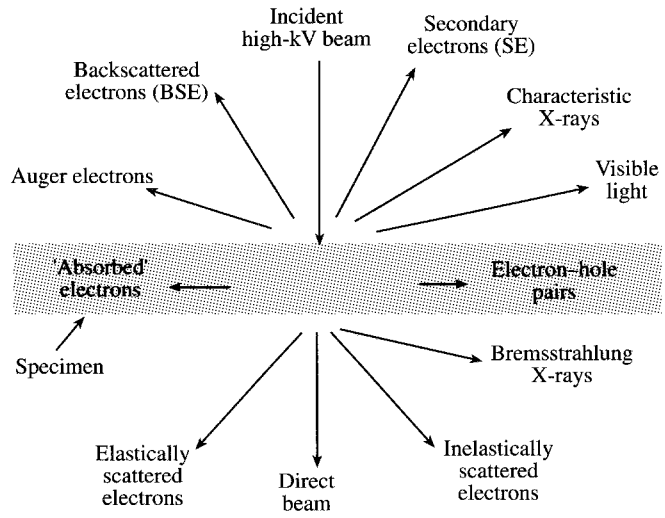
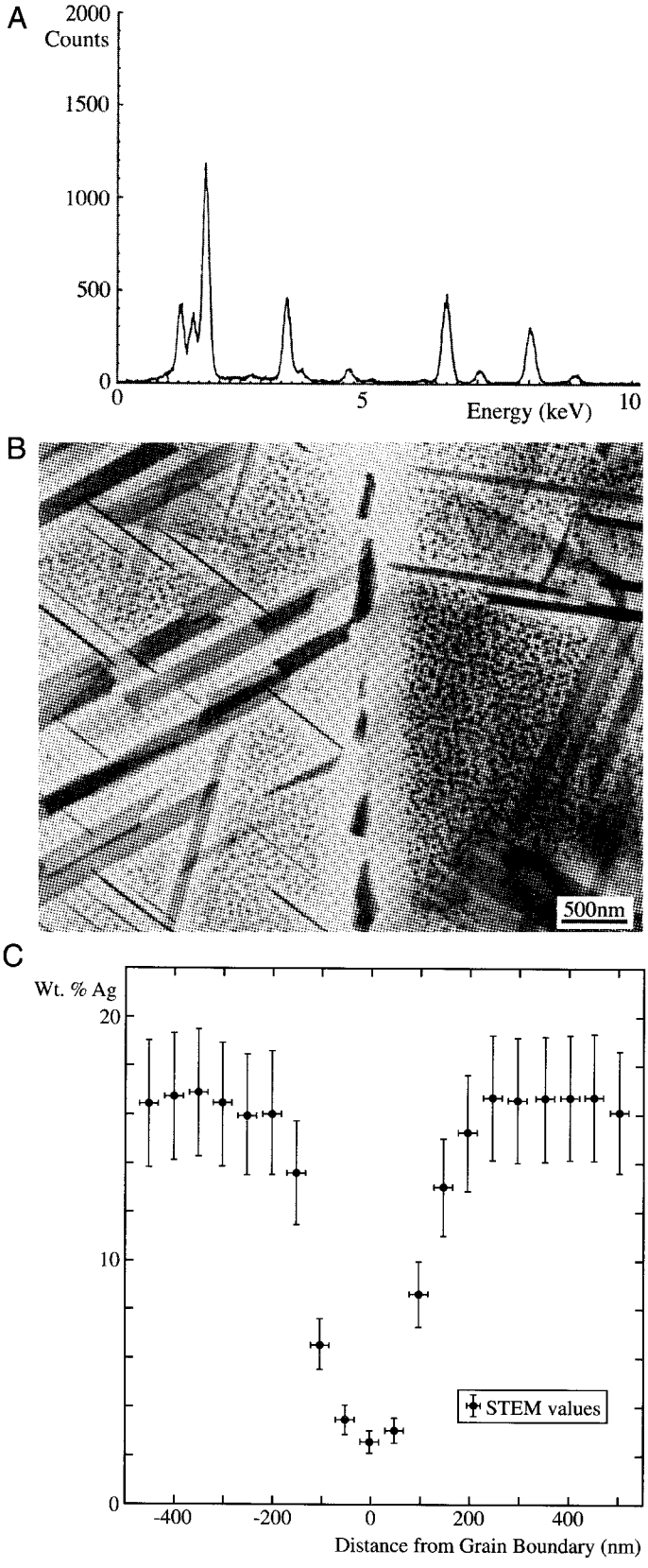


Figure 1.3. Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM. The directions shown for each signal do not always represent the physical direction of the signal but indicate, in a relative manner, where the signal is strongest or where it is detected.



signal-generating instruments. To localize these signals we need to get our TEM to form a very fine electron beam, typically <10 nm and at best <1 nm in diameter. We accomplish this by combining TEM and scanning electron microscope (SEM) technology to create a scanning transmission electron microscope (STEM). The STEM is both the basis for AEMs and a unique scanning imaging microscope in its own right. In fact there are instruments that are only capable of operating in scanning mode and these are sometimes referred to as "dedicated STEMs," or DSTEMs.

1.1.D. Depth of Field

The depth of field of a microscope is a measure of how much of the *object* we are looking at remains "in focus" at the same time. Like the resolution, this property is governed by the lenses in the microscope. The best electron lens is not a very good one, as we've already mentioned, and has been compared to using the bottom of a Coca-Cola bottle as a lens for light microscopy. To minimize this problem we have to use very small limiting apertures in the lenses, narrowing the beam down to a thin "pencil" of electrons which at most is a few micrometers across. These apertures cut down the intensity of the electron beam, but also act to increase the depth of focus of the images that we produce. Remember that "depth of field" refers to the specimen while "depth of focus" refers to the image.

While this large depth of field is chiefly used in the SEM to produce 3D-like images of the surfaces of specimens with large changes in topography, it is also critical in the TEM. It turns out that in the TEM, all of the specimen is usually in focus at the same time, independent of the specimen topography, as long as it's electron transparent! Figure 1.5 shows a TEM image of some dislocations in a crystal. The dislocations appear to start and finish in the specimen, but in fact they are threading their way through the specimen from the top to the bottom, and they remain in sharp focus at all times. Furthermore, we can record the final image at different positions below the final lens of the instrument and it will still be in focus. Compare this with

Figure 1.4. (A) An X-ray spectrum from a small biotite crystal showing peaks at energies that are characteristic of the elements present in the region that interacts with the electron beam. The major peaks from left to right are for Mg, Al, Si, K, Fe, and the Cu support grid. (B) A TEM image of a precipitate-free zone (PFZ) in an aged Al–16 wt% Ag alloy. (C) The Ag profile across the PFZ in (B), obtained through X-ray spectrometry in the TEM showing the depletion of Ag responsible for the PFZ formation.

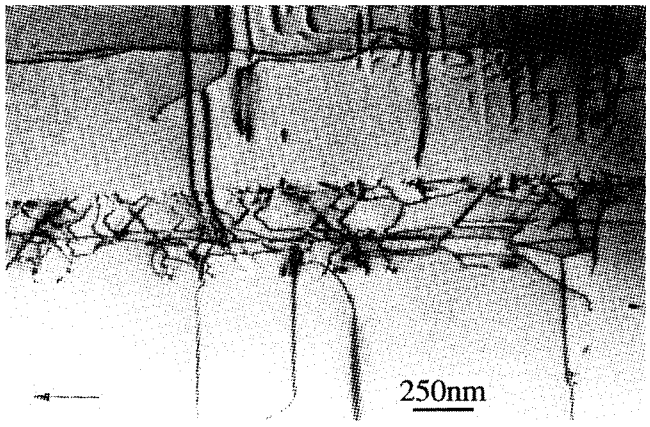


Figure 1.5. TEM image of dislocations in GaAs. A band of dislocations threads through the thin specimen from the top to the bottom but remains in focus through the foil thickness.

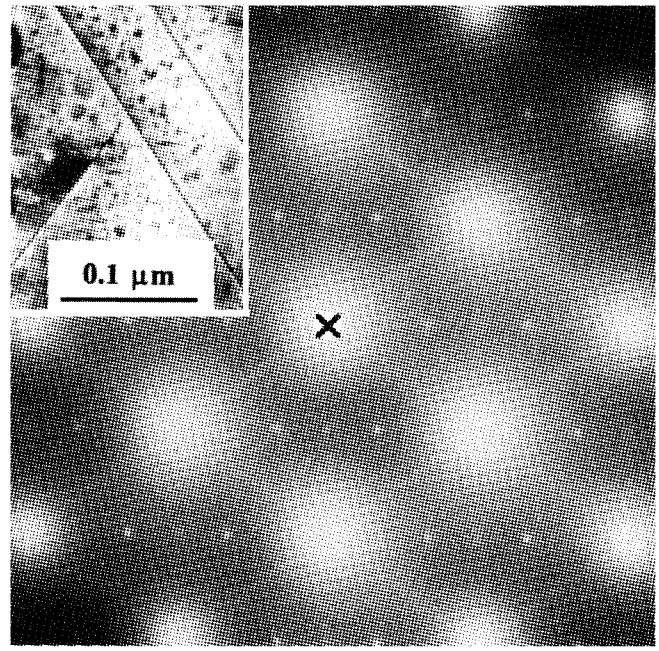


Figure 1.6. TEM diffraction pattern from a thin foil of Al-Li-Cu containing various precipitate phases, shown in the inset image. The central spot (X) contains electrons that come directly through the foil and the other spots and lines are diffracted electrons which are scattered from different crystal planes.

the visible-light microscope where, as you probably know, unless the surface of the specimen is flat to within the wavelength of light, it is not all in focus at the same time. This aspect of TEM gives us both advantages and disadvantages in comparison to the visible-light microscope.

1.1.E. Diffraction

Thompson and Reid showed that electrons could be diffracted when passing through thin crystals of nickel, and the possibility of combining electron diffraction into TEMs was realized by Kossel and Möllenstedt (1939). Today, electron diffraction is an indispensable part of TEM and is arguably the most useful aspect of TEM for materials scientists. Figure 1.6 shows a TEM diffraction pattern which contains information on the crystal structure, lattice repeat distance, and specimen shape, as well as being a most striking pattern. We'll see that the pattern can always be related to the image of the area of the specimen from which it came, in this case shown in the inset. You will also see in Part II that, in addition to the things we just listed, you can conduct a complete crystallographic symmetry analysis of minuscule crystals, including such esoteric aspects as point-group and space-group determination, and at all times the crystallography can be related to the image of your specimen. There is no similar capability on a light microscope because of the relatively large wavelength of visible light.

So an electron microscope can produce atomic level images, can generate a variety of signals telling you about your sample chemistry and crystallography, and you can always produce images that are in focus. There are many other good reasons why you should use electron microscopes. We hope they will become evident as you read through this book. At the same time there are many reasons why you should *not* always seek to solve your problems with the TEM, and it is most important that you realize what the instrument *cannot* do, as well as knowing its capabilities.

1.2. LIMITATIONS OF THE TEM

1.2.A. Sampling

All the above advantages of the TEM bring accompanying drawbacks. First of all, the price to pay for any high-resolution imaging technique is that you only look at a small part of your specimen at any one time. The higher the resolution, therefore, the worse the sampling abilities of the instrument. Von Heimendahl (1980) reported a calculation by Swann in around 1970 estimating that all TEMs, since

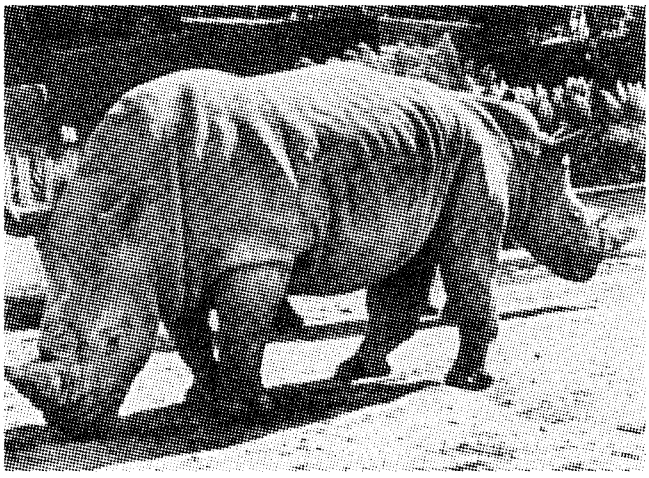


Figure 1.7. Photograph of two rhinos taken so that, in projection, they appear as one two-headed beast. Such projection artifacts in reflected-light images are easily discernible to the human eye but similar artifacts in TEM images are easily mistaken for "real" features.

they first became available commercially, had only examined 0.3 mm^3 of material! Extending that calculation to the present time at best doubles the volume to 0.6 mm^3. So we have an instrument that is a terrible sampling tool. This only serves to emphasize that before you put your specimen in the TEM you must have examined it with techniques that offer poorer resolution but better sampling, such as your eyes, the visible-light microscope, and the scanning electron microscope. In other words, know the forest before you start looking at the leaves on the trees.

1.2.B. Interpreting Transmission Images

Another problem is that the TEM presents us with 2D images of 3D specimens, viewed in transmission. Our eyes and brain routinely understand reflected light images but are ill-equipped to interpret TEM images, and so we must be cautious. Hayes (1980) illustrates this problem well by showing a picture of two rhinos, side by side such that the head of one appears attached to the rear of the other (see Figure 1.7). As Hayes puts it: "when we see this image we laugh" (because we understand its true nature in 3D) "but when we see equivalent (but more misleading) images in the TEM, we publish!" So beware of artifacts, which abound in TEM images.

One aspect of this particular drawback is that, generally, all the TEM information that we talk about in this book (images, diffraction patterns, spectra) is *averaged through the thickness of the specimen.* In other words, a single TEM image has no depth sensitivity, as is apparent from Figure 1.5. So other techniques which are surface-sensitive or depth-sensitive, such as field ion microscopy, scanning-probe microscopy, Auger spectroscopy, Rutherford backscattering, etc., are necessary complementary techniques if you want a full characterization of your specimen.

1.2.C. Electron Beam Damage and Safety

A side effect of ionizing radiation is that it can damage your specimen, particularly in materials such as polymers and some ceramics. Some aspects of beam damage are exacerbated at higher voltages and, with commercial instruments offering up to 400 kV, beam damage now limits much of what we can do in the TEM, even with refractory metals. Figure 1.8 shows an area of a specimen damaged by high-energy electrons. The combination of high-kV beams with the intense electron sources that are available means that we can destroy almost any specimen, if we are not careful. At the same time comes the danger that should *never* be forgotten, that of exposing yourself to ionizing radiation. Modern TEMs are remarkably well engineered and designed with safety as a primary concern, but *never* forget that you are dealing with a potentially dangerous instrument that generates radiation levels that could kill you. So *never* modify your microscope in any way without consulting the manufacturer and without carrying out routine radiation leak tests. If in doubt, don't do it!

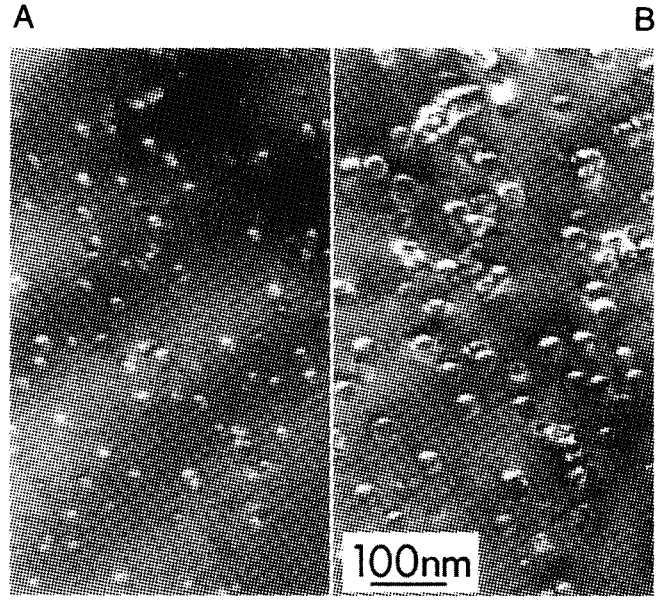


Figure 1.8. Beam damage in quartz after bombardment with 125-keV electrons. With increasing time, from (A) to (B), the damaged regions increase in size.