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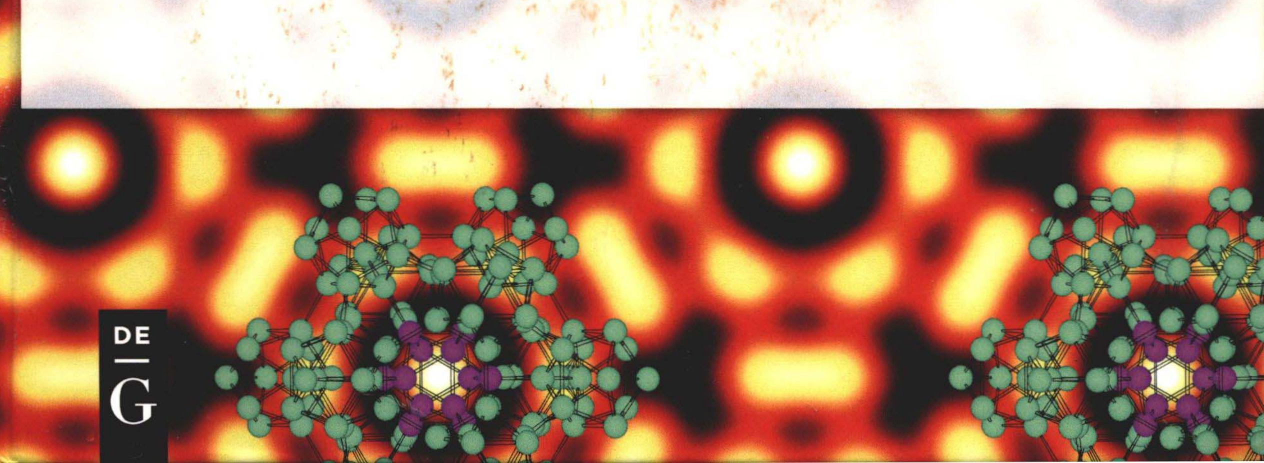
STRUCTURE ANALYSIS OF ADVANCED NANOMATERIALS

NANOWORLD BY HIGH-RESOLUTION ELECTRON MICROSCOPY



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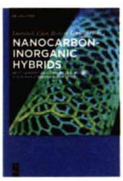

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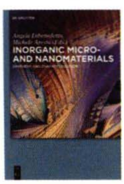

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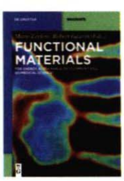

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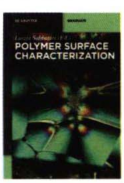

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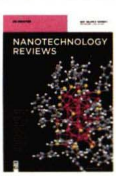

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Preface

Transmission electron microscopes (TEM) are a powerful apparatus for structural analysis. Although many research groups have their own electron microscopes recently, lots of researchers and PhD students are not able to operate the electron microscope and analyze the data efficiently and perfectly, which would be due to the complicated TEM operation and complicated analysis of the actual TEM data.

Although various excellent specialized books for TEM have been published, yet there are not many books for TEM beginners. This book is for the TEM beginners who would like to operate TEM, overview the TEM, take pictures, and analyze the TEM data. When we see the specialized book for TEM, there are many mathematical equations and complicated imaging principles in the book, which is a little high hurdle for a TEM beginner. In this book, the complicated mathematical equations were reduced as little as possible, and the book is focused on the actual views of TEM data and analysis.

This book would be helpful for beginners who would like to observe and analyze the samples in front of them. Recently, several companies can supply TEM photographs by their technique with a charge, and many researchers would make use of them. Sometimes, it is a good idea to ask the professional companies to prepare the TEM samples and to take TEM images with paying. If we ask the professional companies, the money, effort, and time can be saved, comparing with the money, effort, and time to purchase an electron microscope, to educate good TEM operators, and to obtain the TEM data. Such means can be suggested if the purpose and time are restricted and limited. However, it should be noted that the researchers should have clear eyes that can grasp the quality of the TEM data. It is important for them to see many examples of the actual TEM analysis, to analyze by themselves, and to distinguish the quality of the TEM data, in addition to learning the complicated principles of TEM. For them, necessary things would not be the complicated operation technique but understanding the analysis method of the TEM data.

Of course, it is mandatory for researchers, who would like to obtain and analyze the TEM data perfectly, to understand the basic principles of TEM by reading many specialized good books. Reference books would be useful for the researchers who would like to understand and study the TEM in details. However, many students and researchers are under the pressure of necessity to understand their own TEM data and to extract necessary information for them as soon as possible instead of perfect understanding the TEM principles. It is much obliged for the author if this book is helpful for them.

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March 2014, Takeo Oku

Table for physical constants

Physical constants	Symbol	Values	SI units
Velocity of light	c	2.99792458×10^{8}	ms^{-1}
Planck constant	h	6.62607×10^{-34}	Js
Dirac constant	$\hbar = h/2\pi$	1.05457×10^{-34}	Js
Gravitational constant	G	6.67384×10^{-11}	$m^3 s^{-2} kg^{-1}$
Electron charge	e	1.60218×10^{-19}	As (C)
Electron mass	m_e, m_0	9.10938×10^{-31}	kg
Proton mass	m_p	1.67262×10^{-27}	kg
Neutron mass	m_n	1.67493×10^{-27}	kg
Electron energy	$m_e c^2$	0.5110	MeV
Compton wavelength	λ_c	2.4263×10^{-12}	m
Boltzmann constant	k, k_B	1.38065×10^{-23}	JK^{-1}
Magnetic permeability	$\mu_0 = 4\pi \times 10^{-7}$	1.25664×10^{-6}	Hm^{-1} (NA^{-2})
Dielectric constant	$\varepsilon_0 = 1/\mu_0 c^2$	8.85419×10^{-12}	Fm^{-1} (NV^{-2})
Avogadro constant	N_A	6.02214×10^{23}	mol^{-1}
Gas constant	$R = kN_A$	8.31446	$JK^{-1}mol^{-1}$

Physical constants	Symbol	Values and units
Ångström	Å	$0.1\,nm = 10^{-10}$ m
Electron volt	eV	1.60218×10^{-19} J
Wavelength of 1 eV photon	λ	1239.84 nm
Standard atmosphere	atm	1.01325×10^{5} Pa

Contents

1 Introduction

1.1 Characteristic of electron microscopy

Each matter around us consists of atoms. The atoms consist of atomic nuclei and electrons. Electrons were discovered by Joseph John Thomson in 1897. It is believed that electrons are elementary particles which cannot be decomposed further. The size of electron is below 10^{-18} m. Ernest Rutherford discovered atomic nucleus and proton in 1911 and 1919, respectively. After that, neutrons were discovered by James Chadwick in 1932, and a basic model of atom is established. The size of atomic nucleus is 10^{-15} m. Murray Gell-Mann proposed the quark model in which protons and neutrons consist of up quark and down quark.

In this book, main topics are to observe "atoms" which are atomic nucleus with electrons around the nucleus. Electrons exist as electronic cloud around the atomic nucleus, as shown in Figure 1.1. A size of atom is ~ 0.2 nm which is the average size of electron cloud with high existing probability.

How can we observe such atoms? At first, we can think about optical microscopes which are often used in the lessons in elementary schools. For the optical microscopy, images of objects are magnified by optical lens and light. However, wavelengths of the visible light are in the range of 400 and 700 nm, and it is difficult to observe the atoms with the smaller size.

Is there anything with shorter wavelengths compared to visible light? One of the candidates is electrons. For example, the wavelength of electron is 0.000736 nm when the accelerating voltage is 1250 kV. Electrons have very short wavelengths, and they seem to be used for the observation of atoms. Electron microscopes are apparatuses which enlarge the images of matter in atomic scale by electrons. Although optical microscopes are small devices, electron microscopes are larger scale apparatus compared to optical microscopes. Figure 1.2 shows a high-voltage, high-resolution electron microscope with an accelerating voltage of 1300 kV and a point resolution of 0.1 nm. Each atom can be observed by this electron microscope. The size of this electron microscope is over 10 m, and the special building is needed for it.

To investigate atomic arrangements, other methods such as X-ray diffraction and neutron diffraction are used, and especially, X-ray diffraction is widely used in many research laboratories. For these diffraction methods, X-ray or neutron beam are irradiated to specimens, and diffracted beams are analyzed. However, atomic arrangements are not observed directly, and information on atomic arrangements can be obtained by detailed analysis of the diffracted beams. A difference between these diffraction methods and electron microscopy is that we can observe the atoms "directly" by electrons transmitted through the specimens. Figure 1.3 is a high-resolution electron microscope image of thallium-based superconducting oxides. Each

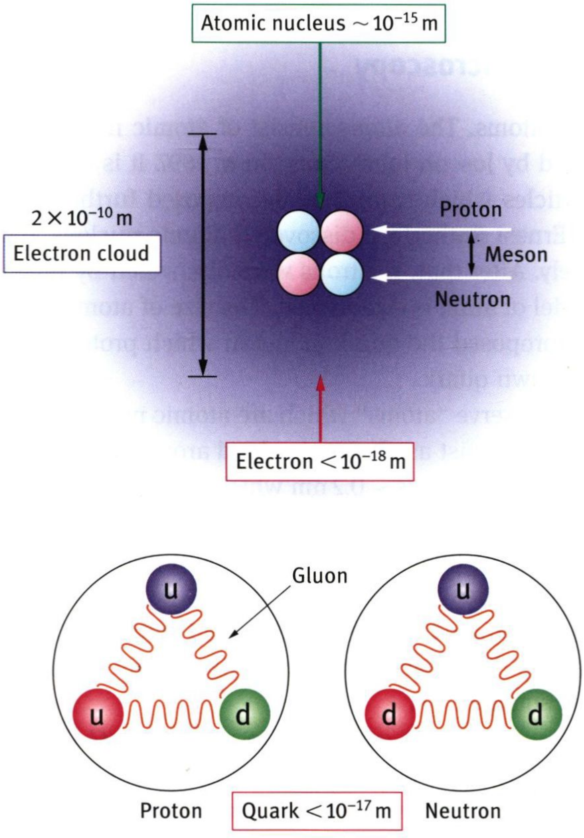

Fig. 1.1: Structure of atom.

dark dot corresponds to metal atoms, and thallium (Tl), barium (Ba), and copper (Cu) atoms are clearly observed. Since atoms can be directly observed by electron microscopes, the electron microscopy is a very useful tool for structural analysis.

1.2 What information can be obtained by electron microscopy?

Information obtained by transmission electron microscopy is as follows:

- Outline of sample: size, shape, etc.
- Crystal structure: atomic arrangement, space group, etc.
- Disordering of atomic arrangement: defect, dislocation, surface, interface, etc.
- Electronic state: binding state between atoms
- Composition: atomic composition ratio of sample
- Magnetic flux: lines of magnetic force

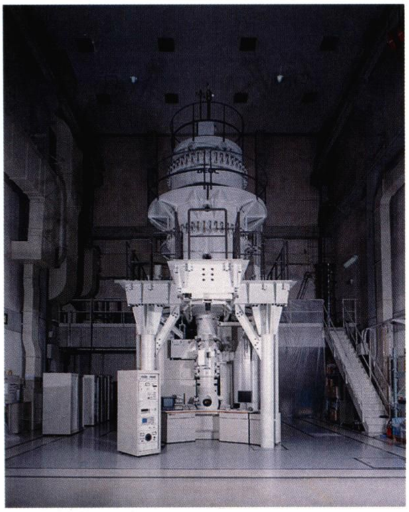

Fig. 1.2: High-voltage, high-resolution electron microscope (JEOL, www.jeol.co.jp/en/).

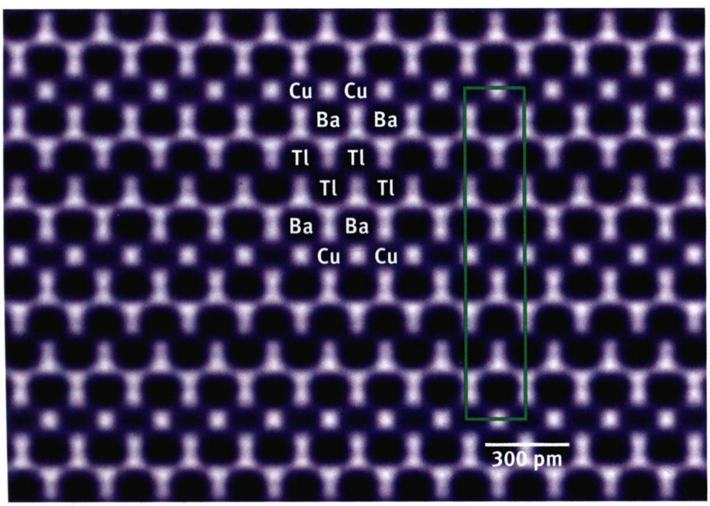

Fig. 1.3: High-resolution image of $Tl_2Ba_2CuO_6$ superconducting oxide.

In the nanotechnology field, structure analysis in atomic scale is mandatory. X-ray and neutron diffraction are also used for the analysis, and they are summarized as listed in Table 1.1.

Characteristics for high-resolution electron microscopy (HREM) are as follows.

(1) Since atomic and unit cell arrangements can be observed by the HREM directly, complicated, unknown structures, which cannot be analyzed by X-ray and neutron diffraction, can be analyzed directly.
(2) X-ray and neutron diffraction methods are suitable to obtain information on averaged atomic arrangements since they are information measured on reciprocal

Table 1.1: Methods for structure analysis.

Method	Radiation rays	Interaction	Wavelength (nm)	Measurement
X-ray diffraction	Electromagnetic wave	Electron cloud	0.15418 (40 kV)	Reciprocal lattice
HREM & electron diffraction	Electron	Electric field	0.000736 (1250 kV)	Real space and reciprocal lattice
Neutron diffraction	Neutron	Atomic nucleus	0.2 (0.02 eV)	Reciprocal lattice

space. However, HREM is more suitable to obtain information on local atomic arrangements such as defect, surface, interface, cluster, and nanostructure with 5-fold symmetry.

(3) Atomic structures can be solved in the crystallographic way using intensities and phases of the structure factors. Only intensity data of structure factors (square of amplitudes) can be obtained by diffraction methods using X-ray, neutron and electron, and phase information is not included in the data. On the other hands, phase information can be extracted from Fourier transform of HREM images.

Fields for interaction are also different. As listed in Table 1.1, X-ray, neutrons and electrons interact with electron cloud, atomic nucleus and electric field (potential), respectively. Methods for structure analysis can be selected in proportion to the purpose. Since electrons interact with matter millions times stronger than X-ray, crystals with extremely small size of nanometer scale can be analyzed, and a small amount of sample is enough for the structure analysis. Many of recent important materials have nanostructures, and electron beam is very effective for the structure analysis of these nanomaterials. By the development of electron gun, lens, detectors, and software, various information of nanodiffraction, electron energy loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDX), and holography are combined together to elucidate atomic arrangements, composition, electronic states, and magnetic structure, simultaneously.

Although various information on materials can be obtained simultaneously by electron microscopy, there are some weak points. Since specimens are set in vacuum in electron microscopes to irradiate electron beam on the specimens, it is difficult to observe liquid and vapor, and living things cannot be observed as it is. Since the electron beam has high energy, sensitive samples such as organic materials are damaged by the electron beam. In addition, elements with small atomic number such as hydrogen have weak interaction with electron beam, and it is difficult to detect the atoms directly. In spite of these weak points, electron microscopy is very attractive apparatus to give us various atomic information in nanoworld. Details of the transmission electron microscopy (TEM) are described in Refs. [1–9].

1.3 Various types of electron microscopy

Various types of electron microscopy are used according to the purpose. Here, various types of electron microscopes and microscopy methods are introduced. The electron microscopy means a method for observation and analysis of various signals coming out from the sample when electron beams are irradiated.

1.3.1 Transmission electron microscope

Transmission electron microscope (TEM) is a most widely used electron microscope. Electron beams are irradiated on a sample, and transmitted electrons through the sample are focused and imaged under the sample. Since the image can be enlarged over several 10,000 times, microstructures can be directly observed. The word "TEM" seems to acquire citizenship among material scientists.

1.3.2 Electron diffraction

One of the important characteristics of electron microscopes is that it is possible to obtain electron diffraction (ED) showing averaged atomic arrangements at the same nanoscopic scale view.

1.3.3 High-resolution electron microscope

High-resolution electron microscope (HREM) is an apparatus that the resolution of TEM is enhanced up to $\sim$ 0.2 nm. Atomic arrangements and nanostructures can be directly observed by the HREM, and the HREM is a main subject in this book.

1.3.4 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX or EDS) is a method for composition analysis. By measuring energies of characteristic X-rays radiating from the observed region, the element can be identified and the atomic composition of the sample can be clarified.

1.3.5 Electron energy-loss spectroscopy (EELS)

The element and atomic composition of the sample can be identified by measuring the loss energies of inelastic scattered electrons at the observed regions. In addition, information on electronic states can be obtained.

1.3.6 Energy filtering TEM (EF-TEM)

Two-dimensional distribution of elements and binding states can be directly observed by electron energy-loss spectroscopy (EELS) using the energy difference of transmitted electrons.

1.3.7 Lorentz microscopy

Lorentz microscopy is a method to observe magnetic domains in ferromagnetic samples by TEM. The magnetization of the sample affect electron beams to generate Lorentz force, which results in changing the image contrast in the sample.

1.3.8 Electron holography

Magnetic and electric fields around the sample can be directly observed by reconstructing the interfered electron beams utilizing the coherency of electron waves.

1.3.9 C_s corrected TEM

A negative spherical aberration coefficient (C_s) to cancel positive C_s of the magnetic lenses of the microscope is produced by the C_s corrector, which achieves higher resolution TEM images.

1.3.10 In-situ observation

Change of the sample can be observed continuously at nanoscale, during cooling (−269°C) or annealing (~1000°C), reaction with various vapor, and addition of electricity or physical stress in the electron microscope.