Elastic and Inelastic Scattering in Electron Diffraction and Imaging

Introduction

Diffraction and imaging of transmitted high-energy electrons are important experimental techniques for determining crystal structures. The steady improvement of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and their associated analytical techniques has made it possible to perform structural determination at atomic resolution. The recently commercialized charge-coupled device (CCD) camera and the electron energy filter open a new era in quantitative electron microscopy. With these attachments, the images and diffraction patterns formed by electrons with distinct energy-losses can be separated and digitally recorded. In practice, quantitative data analysis entirely depends on theoretical simulations. This book is about the theories and techniques of elastic and inelastic electron diffraction and imaging and their applications in quantitative electron microscopy. In particular, attempts have been made to summarize and develop the various dynamical theories developed over years from the studies of elastic and inelastic electron multiple scattering, and to apply them for exploring new experimental techniques.

There are many excellent books dedicated to the various techniques associated with TEM. The book by Hirsch et al. (1977) is a fundamental text book for conventional TEM, particular diffraction contrast imaging. The book by Reimer (1984) is more associated with the physics of TEM. The book by Cowley (1981) is the only book which gives a systematic description of the unified theory of electron, neutron and x-ray diffraction. A recent book edited by Buseck et al. (1989) gives a full coverage of high resolution transmission electron microscopy and associated applications in various fields. The books by Spence and Zuo (1992) and edited by Cowley (1992, 1993) are dedicated to electron diffraction techniques. The books on electron energy-loss spectroscopy (Egerton, 1986) and energy dispersive x-ray microanalysis are more related to the analytical applications of TEM. It is apparent that the subjects associated with TEM are rather diverse and each book could only describe a small portion of these topics.

Diffraction and imaging theories of transmitted electrons is an important part of TEM. In most of the existing books, elastic scattering theory is usually described and in some cases the kinematical scattering approach is adopted. The Bethe's elastic scattering theory was comprehensively reviewed by Humphreys (1979). Elastic scattering multislice theory was extensively summarized by Van Dyck (1985). Recently, an excellent review was given by Amelincks and Van Dyck (1993) on the theory of diffraction contrast imaging. The inelastic scattering, however, is usually treated as an "absorption" effect, which is included in the theory by introducing an imaginary potential. The book by Ohtsuki (1983) is more dedicated to inelastic excitations of charged particles, but diffraction and imaging of inelastically scattered electrons are not extensively covered. Therefore, there is a need for a comprehensive summary of the following subjects which are important in quantitative data analysis.

1. Dynamical elastic scattering theories. Elastic electron diffraction is usually approached based on the convenient theoretical scheme for the specific subject of the book, such as Bloch wave theory for convergent beam electron diffraction and multislice theory for high resolution TEM image simulation. But there is lack of a systematic description for all the existing elastic scattering theories.
2. Reflection high-energy electron diffraction (RHEED). RHEED has been an important technique for observing in-situ surface structure evolution in thin film growth. But the quantitative analysis of RHEED patterns is far from satisfactory. Thus it is necessary to summarize the dynamical approaches and to compare them for quantitative RHEED data analysis.
3. Absorption effect. Inelastic scattering is usually considered as an "absorption effect" when one is considering elastically scattered electrons, and it is phenomenologically represented by an imaginary potential. However, no systematic description of the theoretical basis and the related calculations of the absorption potential due to various inelastic scattering processes has been given. These calculations are important in quantitative electron diffraction and imaging.
4. Diffraction of inelastically scattered electrons and the resulting Kikuchi patterns. The theory of inelastic electron diffraction is complex and difficult because of the incoherent scattering

characteristics of the inelastic electrons and, thus, is rarely discussed in the existing books. However, inelastic electron scattering is a subject that has been studied for more than three decades, it is necessary to have a book which summarizes all the existing theoretical achievements. Although the contribution of electrons with energy-loss greater than a few eV can be removed from the diffraction pattern by an energy filter, the phonon scattered electrons remain because of small energy-loss ($<$ 0.1 eV).

5. New imaging techniques using the inelastically scattered electrons. In recent years, great interest has developed in structural determination using inelastically scattered electrons. High-angle annular dark-field imaging in STEM, for example, is based on the signal of high-angle phonon scattered electrons. This imaging technique may provide atomic number sensitive structural information with resolution better than conventional bright-field imaging.

The ultimate goal of electron microscopy is to quantitatively determine the structure of materials. This process will rely on the use of the best possible theory, together with energy filtered high resolution diffraction patterns and images. It is anticipated that electron diffraction and imaging will become as indispensable as x-ray and neutron diffraction for materials research, a status it has not yet achieved. This book focuses on the dynamical diffraction and imaging of elastically and inelastically scattered electrons, and their applications for structural determinations, with particular emphasis on those topics outlined above.

The book is written based on the principles listed below. First, since elastic scattering theory has been described in various books, the diffraction and imaging of inelastically scattered electrons are the main emphasis of this book. Second, all theoretical derivations are initiated from first principles wave mechanics for high-energy electrons ($E_0 > 20$ keV). Elastic scattering is initiated from Schrödinger equation, and inelastic scattering is determined by the solution of coupled Yoshioka's equations. Third, since the interaction between incident electrons and crystals is very strong, all the approaches presented are dynamical theories. Fourth, all the theories are linked one with another and are presented in the forms best suited for numerical calculations. All the mathematical operations are given in detail so that the book is self contained. The entire text is linked together and is a unity built on the base of the first principles. Finally, all the physical quantities are defined in SI units, except where stated. For example, Angstrom (Å) is used occasionally for convenience.

This book consists of two parts. Part A is dedicated to the diffraction and imaging of elastically scattered electrons, and takes 1/3 of the text. In chapter 1, fundamental concepts related to electron diffraction are introduced based on the kinematical scattering approach. Some basic quantities are defined and illustrated. This chapter is addressed first for the convenience of discussion in the rest of the book. A comprehensive quantum mechanical description of elastic transmitted electron scattering is given in chapters 2-3. Chapter 2 describes the Bloch wave theory (or Bethe theory) and its applications in convergent beam electron diffraction, diffraction contrast imaging, and weak beam imaging. Chapter 3 gives the wave mechanics basis of the Cowley-Moodie (1957) multislice theory and its applications for simulating high resolution electron microscopy images. Substantial discussion is given to illustrate the methods for introducing high order Laue zone reflections in the multislice calculations. The real space multislice theory is also introduced. In addition to introducing the other existing dynamical theories, the equivalence among these theories are proved in chapter 4. All the existing theories are compared in order to exhibit their uniqueness and disadvantages for treating particular problems. As an important part of high energy electron diffraction, chapter 5 is dedicated to the dynamical theories of RHEED from bulk crystal surfaces. Various theoretical approaches are derived and compared with each other. This is the only comprehensive review of RHEED theories so far.

Part B of this book is dedicated to inelastically scattered electrons, and it takes 2/3 of the text. This is the first book which gives a full discussion of inelastic scattering in electron diffraction. The main contents are listed below.

1. In chapter 6, the imaginary potential introduced in numerical calculation is formally derived from the Yoshioka's coupled equations. The inelastic scattering processes, including phonon excitation, valence excitation and atomic inner-shell (or single-electron) excitation, have been

described in detail. The contribution to the absorption potential made by each process is calculated. The fundamental features of inelastic scattering are illustrated. The effect of electron diffraction on x-ray emission is described. The contents of this chapter are crucially important for quantitative data analysis in practice.

2. Chapter 7 gives the classical diffraction theory of thermal diffusely scattered electrons. A full description on the basis of the "frozen" lattice model is given. Multi-phonon and multiple-phonon excitations are discussed in detail. Finally, the diffuse scattering produced by Huang scattering is introduced.

3. Chapter 8 presents the Bloch wave theory of inelastically scattered electrons. The theory is then extended to the cases of imperfect crystals. This approach is more convenient for calculating Kikuchi patterns. The Bloch wave theory of double-inelastic scattering is also given.

4. The reciprocity theorem, as will be used in chapter 10, is introduced in chapter 9. The equivalence of TEM and STEM is proved. An equivalent theorem for inelastically scattered electrons is derived. The Green's function method is a formal theory for solving electron scattering problem (chapter 10). The theory normally has no restriction on the shape of the crystal, and can be conveniently applied to treat the phonon - atomic inner-shell, double-inelastic scattering. This theoretical scheme makes it possible to evaluate the scattering intensities from crystal lattices of different thermal vibration configurations before numerical calculation. The Green's function approach is believed to be the method best suited for thermal diffuse scattering.

5. In chapter 11, the multislice theory and real space multislice theory of inelastically scattered electrons are given. Detailed applications are shown for simulating the atomic number sensitive images formed by thermal diffusely scattered electrons in STEM and TEM. Extensive discussion is given to cover the characteristics of the "Z-contrast" imaging techniques. This chapter demonstrates the multislice calculations of inelastic electrons in perfect and imperfect crystals. Chapter 12 introduces a simplified multislice theory, which is more convenient for calculations of the diffraction patterns produced by phonon scattered (or thermal diffusely scattered) electrons. The theory is derived based on some simplified model of elastic re-scattering after inelastic excitation, so that the required number of numerical calculations is greatly reduced. The theory is also applicable to

calculation of the streaks in electron diffraction patterns due to phase coupling between atom vibrations. A simple rule is given for identifying the streak directions.

6. Inelastic scattering in electron diffraction makes an unavoidable contribution to high resolution TEM images. Valence-loss and phonon scattering are the two main sources. Chapter 13, thus, specially addresses the calculation of HRTEM images formed by the inelastically scattered electrons. Various cases involving surfaces and interfaces are illustrated. Also the effect of thermal diffuse scattering (TDS) in high-resolution off-axis electron holography is investigated.

7. In electron diffraction, multiple inelastic scattering is always involved if the specimen is thick. Chapter 14 is thus designed to address this problem. Some simple theories are first illustrated. Then the one-particle density matrix theory is introduced, which is powerful for treating the cases involving multiple-elastic and multiple-inelastic scattering.

8. Chapter 15, as the last chapter, is devoted to consider the effect of heat exchange between the crystal and the environment on the scattering behavior of electrons. This is a practical problem, because the crystal being examined is always in contact with the microscope. The possible effects caused by this energy fluctuation process are shown for the cases involving TDS.

Therefore, this book is intended to summarize and develop the theoretical system regarding the diffraction and imaging of elastically and inelastically scattered electrons. Emphasis is placed upon those advanced topics that have not been systematically described in any existing books. This book is addressed to scientists who are interested in quantitative electron microscopy in the areas of condensed matter physics, materials science, surface science, solid state chemistry, mineralogy, and biological science. It is intended to serve as a complete reference for the physics involved in electron diffraction and imaging.

I have written this book with the strong conviction that the quantitative analysis of energy-filtered elastic and inelastic scattering diffraction patterns and images is the future direction of TEM. On reading the literature, one is struck by the enormous variety of theories, presented in different forms, defined in different unit systems, and derived based on different approximations. It would be a Herculean task to present all the theories in a coherent manner and describe all the subjects based on a unified base, because the dynamical theories, particular if there are inelastic excitations, are mathematically very complex. Thus, to expert in the field, the examples in this book may seem somewhat oversimplified. But my aim is to explain the principles regarding the implication of the theories and to provide all the useful approaches in a consistent format. Apologize is expressed here to those authors whose work may have been overlooked among the many hundreds of papers.