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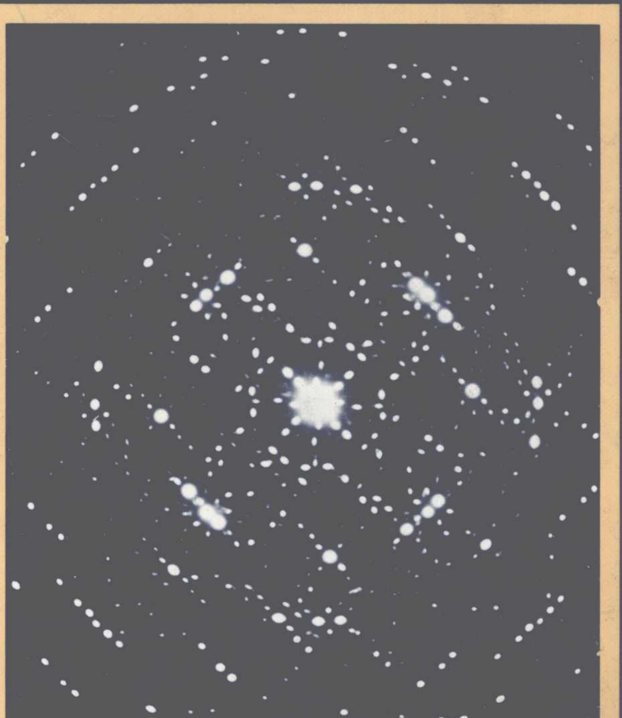
ELECTRON AND ION MICROSCOPY AND MICROANALYSIS

PRINCIPLES AND APPLICATIONS

LAWRENCE E. MURR



ELECTRON AND ION MICROSCOPY AND MICROANALYSIS

Principles and Applications

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SERIES INTRODUCTION

Optical science, engineering, and technology have grown rapidly in the last decade so that today optical engineering has emerged as an important discipline in its own right. This series is devoted to discussing topics in optical engineering at a level that will be useful to those working in the field or attempting to design systems that are based on optical techniques or that have significant optical subsystems. The philosophy is not to provide detailed monographs on narrow subject areas but to deal with the material at a level that makes it immediately useful to the practicing scientist and engineer. These are not research monographs for researchers, although we expect that workers in optical research will find them extremely valuable.

This introduction presents this series' first volume entitled "Electron and Ion Microscopy and Microanalysis: Principles and Applications," by Lawrence E. Murr. This volume is indeed an auspicious start to the series.

In future volumes, we expect to be covering those topics that have been a part of the rapid expansion of optical engineering. The developments that have led to this expansion include the laser and its many commercial and industrial applications, the new optical materials, gradient index optics, electro- and acousto-optics, fiber optics and communications, optical computing and pattern recognition, optical data reading, recording, and storage, biomedical instrumentation, industrial robotics, integrated optics, infrared and ultraviolet systems, etc. Since the U.S. Commerce Department projects the optical industry to be one of the major growth industries for the 1980s, this list will surely become even more extensive.

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PREFACE

This book is part of an evolutionary process that started around 1966. It is an extension and revision of my original book *Electron Optical Applications in Materials Science* published by the McGraw-Hill Book Co. in 1970. In the preface of the original volume, I wrote "During my final year of graduate school I felt a need for a useful, comprehensive treatment of electron microscopy and its related electron optical techniques. I also felt that such a treatment should stress the uses of electron optical theory, phenomena, and devices in the study and characterization of materials. The actual writing began with a fervent desire to teach the basic theory and applications of electron optical devices and techniques, and to create an awareness of the diversity of electron optical uses for the materials scientist". In retrospect, I believe that, to a large extent, I did succeed in my original goals with *Electron Optical Applications in Materials Science*. That book received a number of favorable reviews following publication and was adopted or used by nearly two dozen universities in the United States and by universities in Taiwan, India, South America (particularly Chile and Brazil), and numerous European and other countries during the decade of the 1970s. When *Electron Optical Applications in Materials Science* went out of print in 1978, I received a great deal of encouragement from colleagues who had used the book as teachers, students, or both to consider a revision. I had thought even earlier of the alarming rate at which new concepts were being developed, and the lack of treatment in the original book. At the same time, I was concerned with the importance of the synergism rapidly being promoted and required in many characterization laboratories, not only in analytical electron microscopy, but in the combined approaches to materials characterization involving electron and ion optical techniques.

In the context of what I perceived as the success of the original text and the need to broaden the coverage with a particular aim at developing the analytical concepts underlying the synergism involving both electron and ion optical systems, which were emerging as modern methods of materials characterization, I was sensitive to criticisms leveled by some users who found the original treatment too theoretical, too general, and pitched at a relatively high (graduate) level. Indeed, during my own use of the original McGraw-Hill version through the mid 1970s, I had developed two semester-length courses: one a senior-level course involving fundamentals or elements of electron microscopy and the other a graduate-level course involving electron and ion optical applications.

The actual writing of this book began anew with a fervent desire to teach the basic theory and applications of electron and ion optical devices and techniques and to create an awareness of the diversity of electron and ion optical uses for the scientist or engineer in a wide range of disciplines. I was particularly concerned with the concepts of materials characterization, and I was not concerned that, probably like the original book, this book would be criticized as "taking a physicist's point of view too often". By virtue of the origin and evolution of this book over a period of continuous teaching of courses since 1966, this book is written for students at the senior or graduate level and for self-study by a wide range of materials scientists and engineers, chemists, physicists, metallurgists, ceramists, and others in the physical sciences and engineering who are interested or involved in the study and characterization of materials. It is a textbook designed to offer a program format and act as a reference for at least two semester or two quarter-length courses at the senior or graduate level.

The organization of topics begins with the basic properties of electrons and a short treatment of ions in Chapter 1. The quantum-mechanical aspects of electron optical systems, the characteristic emission properties of electrons from solids, and an explanation of electron emission and field-ion microscopy and related applications are treated in Chapter 2. Chapter 3 deals with the principles of electron and ion optics and the practical uses of an electron or ion optical system. Chapter 4 discusses a broad range of electron and ion probe microanalysis techniques and describes, somewhat synergistically, the basic analytical features of electrons and ions. Chapter 5 considers the electron and ion microscopes and their role in the study of surfaces, and Chapter 6 deals with the theory and applications of electron diffraction. Chapters 7 and 8 cover the principles and applications of conventional and analytical electron microscopy as well as high-voltage transmission electron microscopy; only brief mention is made of the potential uses of transmission ion microscopy in Chapter 7. A wide range of applications is covered, which encompasses high-resolution and *in situ* techniques. The appendices provide easy access to practical data and aids having particular value in electron microscopy.

A list of key references, not intended to be exhaustive, but pointing the way to historical origins or notable applications and contributions, is included at the conclusion of each chapter along with suggestions for supplementary reading. These follow problems, which are for the most part practical, and together with the reference and supplementary readings lists are intended to aid the reader in understanding concepts, applying particular techniques, and solving practical research problems. A section providing solutions and/or discussion of the problems is also appended to the book. I have given special attention to the composition of illustrations and drawings, which are essential to a real understanding of just how certain techniques work, and what kinds of unique applications are possible.

For a good understanding of the bulk of this book, the reader should have a mathematical background equivalent to sophomore-level science or engineering courses, including differential equations and matrix algebra. A course in solid-state physics and x-ray diffraction would also be helpful. The treatment does not assume any rigorous exposure to quantum mechanics. In short, the serious student should have little trouble understanding most of the essentials.

The instructor cannot possibly cover the material in this book in a quarter-length course. At the very least, two semesters or quarters and two separate courses would be required. This book is intended as an aid to the development or teaching of courses in electron microscopy, electron and ion optical applications, or electron and ion microscopy and microanalysis. It cannot be a course syllabus, and it cannot substitute for the classroom or laboratory experience. It can only contribute to that experience. Therefore, the lack of depth at some points in the book must be supplemented with the instructor's own notes or reference materials suggested within or at the conclusion of the individual chapters. This book is an attempt to form a meaningful dialogue between the writer and the reader.

Because this book was written to serve as a multi-purpose text at both the senior and graduate levels, and as a useful reference or self-study resource for the practicing scientist or engineer, some readers may find its style heavy in parts. This may have occurred as a result of my own desire to present the material in a reasonably satisfying way to the student, while still leaving room for the instructor's interpretation and application. The instructor not only has the opportunity to supplement for specific shortcomings, which might be perceived or real, but an obligation to do so if the student is expected to achieve a full understanding. This is not intended to be a "cookbook." To learn to "cook," the student must get into the laboratory and operate the devices and apparatus described. This book will hopefully develop an appreciation for how things work and how they can be applied in an efficient and useful way.

I am indebted to many authors, publishers, and industrial organizations for their kindness in supplying illustrations and data and for their permission to publish them. The various contributions are acknowledged in the text or in appropriate figure captions. I am also grateful for the valuable comments and suggestions tendered by my associates and students as well as other reviewers during the preparation and class testing, revision, and updating, which have gone on for the past 15 years. Jon Orloff was kind enough to critically read the sections on electron and ion optics, and Margaret Day provided numerous editorial comments. I am especially grateful to Elizabeth Fraissinet who spent nearly a year typing this book in camera-ready form. Hers was a dedication beyond remuneration and for which I can only be eternally grateful. The help of Donna Rodriguez and especially Carol Hendrickson in typing the running heads, front matter, and text corrections, and portions of the appendices and index was also a significant contribution, which I gratefully acknowledge. Paul Carlson provided encouragement and other intangibles for which I am also grateful.

Finally, I have appropriately dedicated this book to my wife and children for their continued devotion and encouragement throughout these years.

LAWRENCE E. MURR

CONTENTS

1

FUNDAMENTAL PROPERTIES OF ELECTRONS AND IONS

1.1 INTRODUCTION

In a book proposing to deal with emission or production, operations on, and detection of electrons and ions in one form or another, it would seem desirable at the outset to outline their intrinsic physical properties (and their associated historical development). In addition, it would also seem necessary to deal with the properties of electrons in atoms and solids, and then to describe the production and properties of ions. Indeed, the electron is a remarkable concept; at the risk of sounding melodramatic, it might be said that the electron represents the single most important entity in the universe.

There are two very important intrinsic features associated with electrons, namely, the fact that they are, ideally, negatively charged particles possessing a finite mass; and that an electron, or a beam of electrons, possesses a wave nature akin to that normally associated with light, x-rays, or related electromagnetic radiations.* It is this wave-particle

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In 1932 C. D. Anderson announced the observation of positively charged particles possessing a charge and mass identical to the negative electron. These have since come to be called positrons.

dualism that renders the electron especially suited to investigating the structure and composition of matter in an electron optical device.

The controversy over the wave-particle identity of electrons (cathode rays) reached its peak at the close of the nineteenth century and continued into the first two decades of the twentieth century. The resolution of the apparent wave-particle paradox was essentially found in quantum mechanics perhaps most notably in the form of Schrödinger's equation, the de Broglie "matter wave" concept, the Heisenberg uncertainty principle, and related contributions during the two decades after 1910. In a real sense, the quantum-mechanical treatment of electrons did not resolve the wave-particle dualism solely in terms of a simple particle or wave-train analog. Indeed, the electron must be defined in terms of its inherent features as a fundamental entity.

1.2 ELECTRON CHARGE AND MASS

The pioneering work of M. Faraday had shown, among other things, that in electrolysis a definite amount of material was deposited for every coulomb of electricity that passed through the solution. In 1881 G. J. Stoney recognized the atomic implications of Faraday's laws, and introduced the term electron to designate an elementary charge. It was not until the experiments of Sir J. J. Thomson in 1895 that the term electron was used in its present-day meaning. Since Faraday had shown that 1 g of hydrogen was liberated for each 96,500 coulombs of charge expended (based on an estimate of 10^{25} atoms of hydrogen for each gram weight of hydrogen), Stoney estimated the electronic charge to be roughly 10^{-20} coulomb (0.3×10^{-10} esu). While the method itself was entirely correct, the estimate of charge was not, since the number of hydrogen atoms estimated to compose a gram weight of the same element was in error. It was not until about 1941, in fact, that x-ray determinations showed the number of atoms in a gram atomic weight of an element (Avagadro's number) to be 6.023×10^{23} and thus allowed the correct charge to be computed on the basis originally proposed by Stoney.

The fact that electrification of a rarefied gas produces "cathode rays" whose trajectory is made visible by luminescence and fluorescence, and which are deviated by magnetic or electric fields, was already known as early as 1869. And, Sir W. Crookes about 1886 had even proposed that cathode rays were negatively electrified particles. This point was definitely proven by J. Perrin in 1895 [1]. Simultaneously, in 1895, Roentgen discovered that x-rays were emitted when cathode rays bombarded a metal target.

Two years later, in 1897, Thomson [2] published the first accurate measurements of the ratio of electron charge to mass (e/m), following the experimental proposals introduced by A. Schuster [3] some 10 years before. Thomson's value of 2.3×10^7 emu/g was considerably improved about 1900 in similar experiments by W. Kaufmann [4] who measured $e/m = 1.8 \times 10^7$ emu/g. This latter value is nearly in agreement with the presently accepted value.

$$\frac{e}{m} = (1.758896 \pm 0.000028) \times 10^7 \text{ emu/g}$$

The basis for experimental measurements of e/m is illustrated in the sketch of Fig. 1.1. In this scheme, essentially employed by Kaufmann [4], the cathode ray (electron beam) accelerated in the x direction by the anode potential V_0 enters a transverse magnetic field (acting in the z direction). Each electron in this field is subsequently subject to a force Bev_0 (where B is the magnetic field strength, e the electron charge, v_0 is the average electron velocity), in the y direction. Consequently, the electron beam will deviate from the central axis by an amount depending primarily on the electron velocity and the magnitude of the magnetic field.

In effect, we say that in the field region (shown shaded in Fig. 1.1) the electron path is circular, and defined by the radius of *R*. However, on leaving the field region (at F in Fig. 1.1), the electron trajectory remains a straight line normal to *R*. In the field region we then have

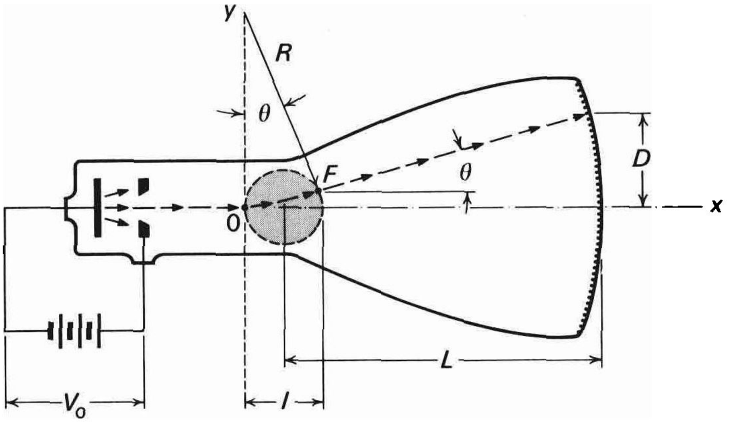

FIG. 1.1 *Magnetic deflection of electrons in cathode-ray tube.*

$$Bev_o = \frac{mv_o^2}{R}$$

and considering

$$eV_o = \frac{mv_o^2}{2}$$

we obtain

$$R = \frac{1}{B}\sqrt{\frac{2mV_o}{e}} \tag{1.1a}$$

Assuming the angle ϕ to be small, we can approximate

$$\theta \cong \frac{\ell}{R}$$

and further assuming $L >> \ell$ we could consider the observed beam deflection D to be

$$D \cong L\theta$$

for small θ. Substituting for θ and R above, and rearranging, then results in the following approximate expression for e/m:

$$\frac{e}{m} = 2V_o\left(\frac{D}{\ell LB}\right)^2 \tag{1.1b}$$

Suffice it to say that Eq. (1.1b) is an approximation that is improved by the patience of the experimentalist. Precision measurements are, however, for the most part not feasible. It was not until studies of the Zeeman effect, about 1935, that a precise value of e/m as presented was obtained. These studies also proved that electrons in a solid were identical to the cathode rays that solids emitted.

It is also instructive to note that if the magnetic field of Fig. 1.1 is replaced with an electric field by inserting square plates of a side, ℓ positioned symmetrically with respect to the central axis of the electron beam in the z plane and in the same position with respect to the cathode-ray tube shown in Fig. 1.1, then the balance of forces in the field region between the plates will become

$$eE = \frac{mv_o^2}{R}$$

where E is the electric field strength, and