PRINCIPLES OF ANALYTICAL ELECTRON MICROSCOPY

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PREFACE

Since the publication in 1979 of *Introduction to Analytical Electron Microscopy* (ed. J. J. Hren, J. I. Goldstein, and D. C. Joy; Plenum Press), analytical electron microscopy has continued to evolve and mature both as a topic for fundamental scientific investigation and as a tool for inorganic and organic materials characterization. Significant strides have been made in our understanding of image formation, electron diffraction, and beam/specimen interactions, both in terms of the "physics of the processes" and their practical implementation in modern instruments. It is the intent of the editors and authors of the current text, *Principles of Analytical Electron Microscopy*, to bring together, in one concise and readily accessible volume, these recent advances in the subject.

The text begins with a thorough discussion of fundamentals to lay a foundation for today's state-of-the-art microscopy. All currently important areas in analytical electron microscopy—including electron optics, electron beam/specimen interactions, image formation, x-ray microanalysis, energy-loss spectroscopy, electron diffraction and specimen effects—have been given thorough attention. To increase the utility of the volume to a broader cross section of the scientific community, the book's approach is, in general, more descriptive than mathematical. In some areas, however, mathematical concepts are dealt with in depth, increasing the appeal to those seeking a more rigorous treatment of the subject.

Although previous experience with conventional scanning and/or transmission electron microscopy would be extremely valuable to the reader, the text assumes no prior knowledge and therefore presents all of the material necessary to help the uninitiated reader understand the subject. Because of the extensive differences between this book and *Introduction to Analytical Electron Microscopy*, the current volume is far more than a second edition. *Principles of Analytical Electron Microscopy* easily stands alone as a complete treatment of the topic. For those who already use the first text, *Principles of Analytical Electron Microscopy* is an excellent complementary volume that will bring the reader up to date with recent developments in the field.

The text has been organized so that it can be used for a graduate course in analytical electron microscopy. It makes extensive use of figures and contains a complete bibliography at the conclusion of each chapter. Although the book was written by a number of experts in the field, every attempt was made to structure and organize each chapter identically. As such, the volume is structured as a true textbook. The volume can also be used as an individual learning aid for readers wishing to extend their own areas of expertise since the text has been compartmentalized into discrete topical chapters.

This preface would be incomplete if we did not acknowledge those who participated directly or indirectly in our efforts. The editors thank the many organizations and individuals who made *Principles of Analytical Electron Microscopy* possible. Without their support and assistance, the project would have never been completed. The Microbeam Analysis Society (MAS) and Electron Microscopy Society of America (EMSA) must be acknowledged for their initial sponsorship, which was essential in the earliest stages of this project. J. I. Goldstein expresses his gratitude for research support from the Materials Science Program of the National Aeronautics and Space Administration and from the Earth Sciences Division of the National Science Foundation. We all appreciate the encouragement and support of AT&T Bell Laboratories. D. C. Joy specifically acknowledges the support of AT&T Bell Laboratories management: L. C. Kimmerling, Manager, Materials Physics Research Department; G. Y. Chin, Director, Materials Research Laboratory; W. P. Schlichter, Executive Director, Materials Science and Engineering Division; and A. A. Penzias, Vice President, Research.

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CHAPTER 1

ELECTRON BEAM–SPECIMEN INTERACTIONS IN THE ANALYTICAL ELECTRON MICROSCOPE

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I. INTRODUCTION

Energetic electrons interact with the atoms and electrons of a specimen in a wide variety of ways, many of which can be used to obtain information when using the analytical electron microscope (AEM). It is the purpose of this chapter to describe the properties of these interactions so as to provide a basis for discussions of imaging and microanalysis in subsequent chapters. Only a cursory examination of the complex subject of electron interactions can be presented. A catalog of equations that describe the various forms of electron scattering will be provided, together with examples of the application of these equations to specific calculations. This "user's guide" to

electron interactions will be accompanied by references to more complete treatments, which enable the interested reader to find additional detail, e.g., Bethe and Ashkin (1953). The separate topic of diffraction contrast will be treated at length in Chapter 9.

II. SCATTERING

The interaction of the beam electrons with the ionic cores of the atoms and loosely bound electrons takes place through various mechanisms of electron scattering, in which the direction and/or energy of the beam electron are changed, with the possibility of the energy transfer to the specimen and the consequent emission of some form of secondary radiation. Two general types of scattering are recognized:

- Elastic scattering—The direction of the electron trajectory is altered, but the energy remains essentially constant.
- Inelastic scattering—The magnitude of the electron velocity is altered, and the kinetic energy ($E = mv^2/2$, where m is the electron mass and v is the velocity) is reduced. Energy is transferred to the atoms of the sample.

Scattering processes are quantified by means of the cross section, σ, which is the probability that a process will occur. The cross section is defined as

$$\sigma = N/n_t n_i \qquad \text{events/e}^-/(\text{atom/cm}^2) \tag{1}$$

where N is the number of events of a certain type (elastic scattering events, inner shell ionizations, etc.) per unit volume (events/cm^3), n_t is the number of target sites per unit volume (atoms/cm^3), and n_i is the number of incident particles per unit area (electron/cm^2). Although cross sections are usually thought of as having dimensions of area (cm^2) and give the effective "size" of an atom, it should be recognized that the dimensionless quantities present in the definition of Eq. (1) are important in properly employing the cross section in a calculation. Thus, the complete dimensions of Eq. (1) are events/electron/(atom/cm^2).

The cross section is often more conveniently used by transforming it into a mean free path, λ, which is the mean distance the electron must travel through the specimen to undergo an average of one event of a particular type. The cross section can be converted into a mean free path by means of a dimensional argument

$$\sigma \frac{\text{events}}{\text{electron(atom/cm}^2)} \times N_0 \frac{\text{atoms}}{\text{mole}} \times \frac{1}{A} \frac{\text{moles}}{\text{g}} \times \rho \frac{\text{g}}{\text{cm}^3} = \frac{1}{\lambda} \frac{\text{events}}{\text{cm}}$$

or

$$\lambda = A/\sigma_i N_0 \rho \qquad \text{cm/event} \tag{2a}$$

where N_0 is Avogadro's number, A is the atomic weight, and ρ is the density. The mean free path for a given type of event, i, is obtained by substituting the appropriate cross section, σ_i, in Eq. (2a). If several different processes, a, b, c, etc., can occur, the total mean free path, λ_t, is found by calculating the mean free paths for the individual processes, λ_i, and combining them according to the equation

$$\frac{1}{\lambda_t} = \sum_i \frac{1}{\lambda_i}. \tag{2b}$$

Alternatively, we can calculate the probability that an event will take place, P (events/e^-). From the argument in Eq. (2a), the probability, P, for a given process is described by

$$P\,(\text{events}/e^-) = \frac{\sigma N_o \rho t}{A} \tag{3}$$

where t is the total specimen thickness.

III. ELASTIC SCATTERING

A. Elastic Scattering Cross Sections

As an energetic beam electron passes near the nucleus of an atom, the electron can be scattered elastically by the coulombic field of the nucleus, a process known as nuclear or Rutherford scattering. According to Wentzel (1927) and Mott and Massey (1965), the differential cross section for Rutherford scattering corrected for relativistic effects and screening of the nucleus by inner shell electrons is

$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{16\,E^2}\,|\sin^2(\theta/2) + (\theta_o^2/4)|^{-2}\,|1 - \beta^2 \sin^2(\theta/2) + \pi\alpha\beta\,[\sin(\theta/2) - \sin^2(\theta/2)]| \tag{4a}$$

where the element of solid angle $d\Omega = 2\pi \sin\theta\, d\theta$, θ is the scattering angle measured relative to the incident electron trajectory, $0 \leq \theta \leq \pi$, Z is the atomic number, E is the beam energy expressed in keV units in all equations, θ_o is the screening parameter, and $\beta = v/c$. β can be conveniently calculated from

$$\beta = |1 - [1 + (E/511)]^{-2}|^{1/2} \tag{4b}$$

where 511 keV is the rest mass of the electron. The screening parameter has been given by Cosslett and Thomas (1964) as $\theta_o = 0.1167\, Z^{1/3}/E^{1/2}$ (radians). The factor, α, in Eq. (4a) (McKinley and Feshbach, 1948) has been given by Mott and Massey (1965) as $\alpha = Z/137$ for light elements. Tabulated values for α appropriate to heavier elements have been given by McKinley and Feshbach (1948). Because the exact cross section given by Eq. (4a) is not reducible to an analytic form due to the term, α, it is often convenient for purposes of estimating cross sections to ignore this factor. The uncertainty that this introduces has been calculated for several elements by Reimer and Krefting (1976), and a figure for germanium taken from their work is shown in Figure 1(a). In general, the magnitude of the deviation of the relativistic Rutherford cross section from the exact Mott cross section is ~20% for Ge at 100 keV, with the deviation varying as a function of angle. The deviation becomes larger for heavier elements and lower beam energies, as shown for gold in Figure 1(b). Reimer and Krefting (1976) have emphasized the importance of using the exact Mott cross section for accurate calculations, especially in the Monte Carlo electron trajectory simulation.

The differential Rutherford cross section can be expressed in the following terms (Bethe and Ashkin, 1953)

$$\sigma_R(\theta) = \frac{e^4 Z^2}{16(4\pi\epsilon_o E)^2}\,\frac{d\Omega}{\left[\sin^2\left(\frac{\theta}{2}\right) + \left(\frac{\theta_o^2}{4}\right)\right]^2} \tag{5a}$$