
Contents

Chapter 1. An Introduction to Electron Energy-Loss Spectroscopy	1
1.1. Interaction of Fast Electrons with a Solid	2
1.2. The Electron Energy-Loss Spectrum	6
1.3. The Development of Experimental Techniques	9
1.3.1. Energy-Selecting (Energy-Filtering) Electron Microscopes	13
1.3.2. Spectrometers as Attachments to Electron Microscopes	14
1.4. Alternative Analytical Methods	16
1.4.1. Ion-Beam Methods	17
1.4.2. Incident Photons	18
1.4.3. Electron-Beam Techniques	19
1.5. Comparisons of EELS and EDX Spectroscopy	23
1.5.1. Detection Limits and Spatial Resolution	24
1.5.2. Specimen Requirements	26
1.5.3. Accuracy of Quantification	26
1.5.4. Ease of Use and Information Content	27
1.6. Further Reading	28
Chapter 2. Instrumentation for Energy-Loss Spectroscopy	31
2.1. Energy-Analyzing and Energy-Selecting Systems	31
2.1.1. The Magnetic-Prism Spectrometer	33
2.1.2. Energy-Selecting Magnetic-Prism Devices	35
2.1.3. The Wien Filter	40
2.1.4. Electron Monochromators	43
2.2. Optics of the Magnetic-Prism Spectrometer	48
2.2.1. First-Order Properties	49
2.2.2. Higher-Order Focusing	56
2.2.3. Design of an Aberration-Corrected Spectrometer	58
2.2.4. Practical Considerations	61
2.2.5. Spectrometer Alignment	63

2.3. The Use of Prespectrometer Lenses	69
2.3.1. Deployment of CTEM Lenses	70
2.3.2. Effect of Lens Aberrations on Spatial Resolution	71
2.3.3. Effect of Lens Aberrations on Collection Efficiency	74
2.3.4. Effect of Lenses on Energy Resolution	76
2.3.5. STEM Optics	78
2.4. Serial Detection of the Energy-Loss Spectrum	80
2.4.1. Design of the Detection Slit	81
2.4.2. Electron Detectors for Serial Recording	84
2.4.3. Noise Performance of a Serial Detector	88
2.4.4. Signal Processing and Storage	90
2.4.5. Scanning the Energy-Loss Spectrum	92
2.4.6. Coincidence Counting	94
2.5. Parallel Recording of the Energy-Loss Spectrum	96
2.5.1. Operation of Self-Scanning Diode Arrays	96
2.5.2. Indirect Exposure Systems	98
2.5.3. Direct Exposure Systems	104
2.5.4. Noise Performance of a Parallel-Detection System	105
2.5.5. Dealing with Diode Array Artifacts	108
2.6. Energy-Selected Imaging (ESI)	113
2.6.1. Postcolumn Energy Filter	113
2.6.2. Prism-Mirror and Omega Filters	116
2.6.3. Energy Filtering in STEM Mode	116
2.6.4. Spectrum-Imaging	119
2.6.5. Elemental Mapping	120
2.6.6. Comparison of Energy-Filtered TEM and STEM	123
2.6.7. Z-Ratio Imaging	126
Chapter 3. Electron Scattering Theory	131
3.1. Elastic Scattering	131
3.1.1. General Formulas	132
3.1.2. Atomic Models	132
3.1.3. Diffraction Effects	137
3.1.4. Electron Channeling	138
3.1.5. Phonon Scattering	141
3.2. Inelastic Scattering	142
3.2.1. Atomic Models	143
3.2.2. Bethe Theory	147
3.2.3. Dielectric Formulation	149
3.2.4. Solid-State Effects	151
3.3. Excitation of Outer-Shell Electrons	154
3.3.1. Volume Plasmons	154
3.3.2. Single-Electron Excitation	165
3.3.3. Excitons	171
3.3.4. Radiation Losses	172

3.3.5. Surface Plasmons	174
3.3.6. Surface-Reflection Spectra	180
3.3.7. Surface Modes in Small Particles	184
3.4. Single, Plural, and Multiple Scattering	185
3.4.1. Poisson's Law	186
3.4.2. Angular Distribution of Plural Inelastic Scattering	188
3.4.3. Influence of Elastic Scattering	190
3.4.4. Multiple Scattering	192
3.4.5. Coherent Double-Plasmon Excitation	193
3.5. The Spectral Background to Inner-Shell Edges	194
3.5.1. Valence-Electron Scattering	194
3.5.2. Tails of Core-Loss Edges	196
3.5.3. Bremsstrahlung Energy Losses	196
3.5.4. Plural Scattering	197
3.6. Atomic Theory of Inner-Shell Excitation	200
3.6.1. Generalized Oscillator Strength	201
3.6.2. Kinematics of Scattering	207
3.6.3. Ionization Cross Sections	210
3.7. Appearance of Inner-Shell Edges	215
3.7.1. Basic Edge Shapes	215
3.7.2. Dipole Selection Rule	221
3.7.3. Effect of Plural Scattering	224
3.7.4. Chemical Shifts in Threshold Energy	225
3.8. Near-Edge Fine Structure (ELNES)	227
3.8.1. Densities of States Interpretation	227
3.8.2. Validity of the Dipole Approximation	230
3.8.3. Molecular Orbital Theory	233
3.8.4. Multiple-Scattering (XANES) Theory	233
3.8.5. Core Excitons	236
3.8.6. Multiplet and Crystal-Field Splitting	237
3.9. Extended Energy-Loss Fine Structure (EXELFS)	238
<i>Chapter 4. Quantitative Analysis of the Energy-Loss Spectrum</i>	245
4.1. Removal of Plural Scattering from the Low-Loss Region	245
4.1.1. Fourier-Log Deconvolution	246
4.1.2. Misell-Jones and Matrix Methods	254
4.1.3. Deconvolution of Angle-Limited Spectra	255
4.2. Kramers-Kronig Analysis	256
4.2.1. Angular Corrections	257
4.2.2. Extrapolation and Normalization	258
4.2.3. Derivation of the Dielectric Function	259
4.2.4. Correction for Surface Losses	261
4.2.5. Checks on the Data	261

4.3. Removal of Plural Scattering from Inner-Shell Edges	262
4.3.1. Fourier-Log Deconvolution	262
4.3.2. Fourier-Ratio Deconvolution	264
4.3.3. Effect of a Collection Aperture	268
4.4. Background Fitting to Ionization Edges	269
4.4.1. Least-Squares Fitting	271
4.4.2. Two-Area Method	272
4.4.3. More Sophisticated Methods	274
4.4.4. Background-Subtraction Errors	274
4.5. Elemental Analysis Using Inner-Shell Edges	277
4.5.1. Integration Method	279
4.5.2. Calculation of Partial Cross Sections	283
4.5.3. Correction for Incident-Beam Convergence	284
4.5.4. MLS Fitting to Reference Spectra	286
4.5.5. Spatial- and Energy-Difference Techniques	287
4.6. Analysis of Extended Energy-Loss Fine Structure	288
4.6.1. Fourier-Transform Method of Data Analysis	288
4.6.2. Curve-Fitting Procedure	297

Chapter 5. Applications of Energy-Loss Spectroscopy 301

5.1. Measurement of Specimen Thickness	301
5.1.1. Log-Ratio Method	302
5.1.2. Absolute Thickness from the K-K Sum Rule	307
5.1.3. Mass-Thickness from the Bethe Sum Rule	310
5.2. Low-Loss Spectroscopy	312
5.2.1. Phase Identification from Low-Loss Fine Structure	312
5.2.2. Measurement of Alloy Composition from Plasmon Energy	316
5.2.3. Characterization of Surfaces, Interfaces, and Small Particles	320
5.3. Energy-Filtered Images and Diffraction Patterns	322
5.3.1. Zero-Loss Images	323
5.3.2. Zero-Loss Diffraction Patterns	326
5.3.3. Low-Loss Images	327
5.3.4. Z-Ratio Images	328
5.3.5. Contrast Tuning and MPL Imaging	329
5.3.6. Core-Loss Images and Elemental Mapping	330
5.4. Elemental Analysis by Core-Loss Spectroscopy	334
5.4.1. Measurement of Hydrogen and Helium	337
5.4.2. Measurement of Lithium, Beryllium, and Boron	339
5.4.3. Measurement of Carbon, Nitrogen, and Oxygen	341
5.4.4. Measurement of Fluorine and Heavier Elements	344
5.5. Spatial Resolution and Detection Limits	345
5.5.1. Electron-Optical Considerations	345
5.5.2. Loss of Resolution due to Elastic Scattering	346
5.5.3. Delocalization of Inelastic Scattering	347
5.5.4. Statistical Limitations	352

5.6. Structural Information from EELS	357
5.6.1. Orientation Dependence of Ionization Edges	357
5.6.2. Core-Loss Diffraction Patterns	361
5.6.3. Coordination from ELNES Fingerprinting	363
5.6.4. Determination of Valency from White-Line Ratios	370
5.6.5. Use of Chemical Shifts	373
5.6.6. Use of Extended Fine Structure	374
5.6.7. Electron-Compton (ECOSS) Measurements	378
5.7. Application to Specific Systems	380
5.7.1. Carbon-Based Materials	381
5.7.2. Polymers and Biological Specimens	388
5.7.3. Radiation Damage and Hole Drilling	391
5.7.4. High-Temperature Superconductors	398
Appendix A. Relativistic Bethe Theory	403
Appendix B. Computer Programs	407
B.1. Matrix Deconvolution	407
B.2. Fourier-Log Deconvolution	410
B.3. Kramers-Kronig Analysis and Thickness Determination	414
B.4. Fourier-Ratio Deconvolution	417
B.5. Incident-Convergence Correction	419
B.6. Hydrogenic <i>K</i> -Shell Cross Sections	420
B.7. Modified-Hydrogenic <i>L</i> -Shell Cross Sections	423
B.8. Parameterized <i>K</i> -, <i>L</i> -, <i>M</i> -, <i>N</i> -, and <i>O</i> -Shell Cross Sections	425
B.9. Lenz Elastic and Inelastic Cross Sections	428
B.10. Conversion between Oscillator Strength and Cross Section	429
B.11. Conversion between Mean Energy and Inelastic Mean Free Path	430
Appendix C. Plasmon Energies of Some Elements and Compounds	431
Appendix D. Inner-Shell Energies and Edge Shapes	433
Appendix E. Electron Wavelengths and Relativistic Factors; Fundamental Constants	437
References	439
Index	481