

B. K. Agarwal

X-Ray Spectroscopy

An Introduction

Second Edition

With 239 Figures

Springer-Verlag

Berlin Heidelberg New York

London Paris Tokyo

Hong Kong Barcelona

Budapest

Contents

1. Continuous X-Rays	1
1.1 Field of a Point Charge Moving with Uniform Velocity	1
1.2 Radiation from an Accelerated or Decelerated Charged Particle	3
1.3 Transverse Radiation Field due to the Acceleration of an Electron to Low Velocity ($\beta < \frac{1}{2}$)	5
1.4 Maxwell's Equations	6
1.5 Coulomb Potential	7
1.6 Retarded Potentials	8
1.7 Lienard-Wiechert Potentials	11
1.8 Radiation from an Accelerated Charge	12
1.9 Radiation at Low Velocities	14
1.10 Polarization of Continuous X-Rays	16
1.11 The Case of \vec{v} Parallel to \vec{v} (Relativistic)	18
1.12 Sommerfeld's Theory for the Spatial Distribution of Continuous X-Rays	18
1.13 Frequency Spectrum of Continuous X-Rays	21
1.14 Experimental Spectral and Spatial Distributions	23
1.15 Shortcomings of Classical Theory	25
1.16 Kramers' Semiclassical Theory	27
1.17 Quantum Mechanical Considerations	38
1.17.1 Born Approximation	39
1.17.2 Sommerfeld's Result	40
1.17.3 Polarization	43
1.17.4 Screening	46
1.18 Bremsstrahlung in Other Processes	46
2. Characteristic X-Rays	51
2.1 Line Emission	51
2.2 Moseley Law	53
2.3 Classical Oscillator Model	54
2.4 Quantum Theory	56
2.5 Ionization Function	57
2.5.1 Classical Theory	57
2.5.2 Quantum Theory	59
2.5.3 Heavy Projectiles	62
2.5.4 Intensity	63
2.5.5 Molecular-Orbital X-Rays	66

2.6	Ratio of Characteristics to Continuous Radiation	66
2.7	X-Ray Terms	67
2.8	Energies of Atomic X-Ray Levels and Energy-Level Diagrams	70
2.9	Electric-Dipole Selection Rules	75
2.10	Relative Intensities of Emission Lines in a Multiplet	77
2.11	Screening and Spin Doublets	79
2.12	Quantum Theory of Spontaneous Emission of X-Ray Lines and Multipoles	89
2.12.1	Spontaneous Electric-Dipole Transition	90
2.12.2	Spontaneous Higher-Multipole Transitions	91
2.13	Parity Selection Rules and Forbidden Lines	92
2.14	Absorption Discontinuities	96
2.15	Comparison of Optical and X-Ray Spectra	101
2.16	Nomenclature of X-Ray Lines	102
3.	Interaction of X-Rays with Matter	105
3.1	Free, Damped Oscillator	105
3.2	Form and Width of Lines	106
3.3	Forced, Damped Oscillator	109
3.4	Complex Dielectric Constant	110
3.5	Refractive Index	112
3.6	Correction of the Bragg Equation	114
3.7	Measurement of Refractive Index	116
3.7.1	The Method of Critical Angle of Reflection	116
3.7.2	The Method of Symmetrical Reflection	117
3.7.3	The Method of Unsymmetrical Reflection	117
3.7.4	The Method of Refraction in a Prism	119
3.8	Absorption of X-Rays and Dispersion Theory	120
3.8.1	Absorption by an Undamped Oscillator	120
3.8.2	Absorption by a Damped Oscillator	122
3.9	Kramers-Kallmann-Mark Theory of Refractive Index	126
3.10	Quantum Theory of Dispersion	129
3.10.1	Oscillator Strength	129
3.10.2	Hönl Theory	134
3.10.3	Variation of X-Ray Atomic Scattering Factor in the Region of Anomalous Dispersion	137
3.11	Quantum Theory of Line Shape and Photoabsorption Curve Shape	140
3.12	Absorption Coefficients	144
3.12.1	Quantum Theory of Photoabsorption	148
3.12.2	Various Attenuation Processes	149
3.13	Absorption-Jump Ratios	150
3.14	Total Reflection	151
3.15	X-Ray Interferometry	153
4.	Secondary Spectra and Satellites	155
4.1	Photoelectric Effect	155

4.2	Quantum Theory of the Photoelectric Effect	156
4.2.1	Born Approximation	156
4.2.2	Shake-up Structure	159
4.3	Experimental Systems	161
4.4	Auger Effect and its Relation to ESCA and X-Ray Spectra . . .	164
4.4.1	Auger Effect and Widths of X-Ray Emission Lines and Absorption Edges	166
4.4.2	Auger Effect and the Intensities of X-Ray Emission Lines	166
4.5	Basic Theory of the Auger Effect	167
4.5.1	The Non-relativistic Theory Based on Direct Interaction of Two Electrons	167
4.5.2	Possible Auger Transitions of the Coster-Kronig Type ($X_i \rightarrow X_f Y$)	169
4.5.3	Auger Transitions and Widths of Levels	172
4.5.4	Auger Transitions and Relative Intensities of <i>L</i> -Series Lines	173
4.6	Detection of Auger Electrons	174
4.7	X-Ray Line Width	176
4.8	Satellites	178
4.8.1	Low-Energy Satellites	183
4.9	Fluorescence	185
4.10	Measurement of Fluorescence Yield	188
4.11	Autoionization and Internal Conversions	192
4.12	Muonic X-Rays	193
5.	Scattering of X-Rays	195
5.1	Classical Theory of Thomson and Rayleigh (Coherent) Scattering	195
5.2	Incoherent (Compton) Scattering	199
5.3	X-Ray Raman and Plasmon Scattering	202
6.	Chemical Shifts in Emission Spectra	207
6.1	Solid-State Effects and Bonding	207
6.1.1	Metallic Bond	207
6.1.2	Ionic and Covalent Bonds	209
6.1.3	Hybridized Orbitals	210
6.1.4	Coordination	213
6.1.5	Ionic Character of Covalent Bonds	214
6.2	Chemical Shifts of Emission Lines	219
6.2.1	Level Shift	223
6.2.2	X-Ray Line Shift	225
6.3	Appearance Potential Spectroscopy	227
6.4	Resonance X-Ray Emission Spectroscopy	229
6.5	Width and Fine Structure of Emission Lines	229
6.6	Anisotropic X-Ray Emission Lines	232
6.7	Nuclear Finite-Size Effects	234

7. Absorption Spectra	237
7.1 Absorption Edge	237
7.2 Nature of the Absorption Spectrum and the White Line	242
7.2.1 White Line	243
7.3 X-Ray Absorption Main Edge Structure	247
7.4 Chemical Shifts of Absorption Edges	251
7.5 X-Ray Absorption Near Edge Structure	253
7.6 Extended X-Ray Absorption Fine Structure	257
7.6.1 History of EXAFS	257
7.6.2 Basic Theory of EXAFS	262
7.6.3 EXAFS Experiment and Form	267
7.6.4 Data Analysis: Fourier Transform	269
7.6.5 Graphical Method for Bond Length	272
7.6.6 Curve Fitting Method	274
7.6.7 E_0 Problem	274
7.6.8 Applications of EXAFS	275
7.7 Isochromats	277
8. Soft X-Ray Spectroscopy	279
8.1 Conventional Sources	280
8.2 The Synchrotron as a Source	282
8.2.1 Theory	283
8.2.2 Angular Distribution	284
8.3 Vacuum Spectrograph	287
8.4 Detectors	288
8.5 Emission Spectra	288
8.6 Absorption-Spectra Recording	297
8.7 Interpretation of Absorption Spectra	298
9. Experimental Methods	303
9.1 X-Ray Tubes	303
9.2 Line-Focus Filament	306
9.3 High-Tension Circuits	307
9.4 Wavelength Units	308
9.5 Plane-Crystal Spectrograph	311
9.5.1 Soller Slit	313
9.5.2 Edge-Crystal Spectrograph	314
9.6 Curved-Crystal Spectrograph	314
9.7 Double-Crystal Spectrometer	319
9.7.1 The Case of Zero Dispersion (Minus Position)	321
9.7.2 The Case of Non-zero Dispersion (Plus Setting)	324
9.8 Use of Ruled Gratings	325
9.9 Detectors	327
9.9.1 Photographic Films	327
9.9.2 Gas-Filled Detectors	327

9.9.3	Scintillation Counter	332
9.9.4	Semiconductor Detector	333
9.10	Energy-Dispersion Spectrometry	336
9.10.1	Pulse-Height Selection	336
9.10.2	Pulse-Height Distribution Curves	337
9.10.3	Automatic Pulse-Height Selection	339
9.11	Non-Dispersive Analysis	340
9.11.1	Selective Excitation Method	340
9.11.2	Selective Filtration Method	341
9.11.3	Other Methods	341
9.12	X-Ray Lasers	342
9.13	Intensity Measurement	343
9.13.1	Characteristic Line Intensity	344
9.13.2	X-Ray Dose	346
Appendix A	Rutherford Scattering for an Attractive Field	347
A.1	Equation of Hyperbola	347
A.2	Rutherford Scattering	348
Appendix B	Bohr's Formula for Energy Loss	349
Appendix C	X-Ray Atomic Energy Levels	351
Appendix D	Electron Distribution Among the Levels of Free Atoms	353
Appendix E	Curves Representing Values of Electron Energies	357
Appendix F	Dipole Sum Rule	359
Appendix G	Screening Effect, According to Slater	361
Appendix H	Electronegativity Scale	365
Appendix I	Common Analyzing Crystals	367
Appendix J	Wavelength Tables	369
References	373
Author Index	401
Subject Index	415