

Contents

Part I Basics of Synchrotron Radiation

1	Introduction to Synchrotron Radiation	3
	Antonella Balerna and Settimio Mobilio	
1.1	Introduction	3
1.2	Storage Rings and Synchrotron Radiation Sources	4
1.3	Synchrotron Radiation Properties	8
1.4	Radiated Power and Time Structure	9
1.5	Angular, Spectral and Intensity Distribution.	12
1.6	Polarization	17
1.7	Spectral Brightness and Emittance	19
1.8	Insertion Devices	20
	References	28
2	Characteristics and Properties of Synchrotron Radiation	29
	Giorgio Margaritondo	
2.1	Introduction: Broad Picture of a Synchrotron Light Source . . .	29
2.2	Relativistic Effects in a Nutshell	31
2.3	Definition of the Main Parameters	34
	2.3.1 Spectral Distribution Features	34
	2.3.2 Total Emission	34
	2.3.3 Brightness	35
	2.3.4 Polarization	37
	2.3.5 Time Features	38
	2.3.6 Coherence Parameters	38
2.4	Bending Magnets	42
2.5	Wigglers	44
2.6	Undulators	44
2.7	Free Electron Lasers	50
	2.7.1 The Gain Length	52
	2.7.2 Infrared FELs Versus X-FELs	53
	2.7.3 The Subtle Effects of Relativity	54
	2.7.4 Saturation	55
	2.7.5 Seeding	57

2.8	Why Are Synchrotron and X-FELs Sources Important?	57
2.9	New Types of Synchrotron-Related Sources	60
2.10	A Few Practical Equations.	61
	References	61
3	Instrumentation at Synchrotron Radiation Beamlines	65
	Giuliana Aquilanti, Lisa Vaccari, Jasper Rikkert Plaisier and Andrea Goldoni	
3.1	Introduction	65
3.2	Beamlines in the Hard X-Ray Range (2000–50000 eV).	69
3.2.1	Hard X-Ray Optics.	70
3.2.2	X-Ray Detectors.	77
3.2.3	Diffraction Beamlines: MCX at Elettra	79
3.2.4	Absorption Beamlines: the XAFS Beamline at Elettra	80
3.3	Soft X-Ray and Vacuum Ultraviolet Beamlines	81
3.3.1	Soft X-Ray Energy Optics.	83
3.3.2	Layout for a Soft X-Ray Energy Beamline	85
3.3.3	Low Energy VUV (4–40 eV) and Visible-Infrared Beamlines	87
3.3.4	Experimental Examples to Test the Beamline Performance.	91
3.4	Cooling of Optics and Other Beamline Parts	94
3.5	X-Ray Optics for Microscopy	95
3.5.1	X-Ray Focusing Optics.	96
	References	102

Part II Fundamental Interactions

4	Introduction to Matter Radiation Interaction	107
	Settimio Mobilio	
4.1	Introduction	107
4.2	Classical Description of Electromagnetic Waves and Their Interaction with the Matter	109
4.2.1	Electromagnetic Waves in the Vacuum.	109
4.2.2	Electromagnetic Waves in Matter.	111
4.2.3	Classical Microscopic Description of the Complex Index of Refraction.	114
4.2.4	The Scattering and its Classical Description	118
4.2.5	Elastic Scattering at High Energy.	119
4.2.6	Anomalous Scattering.	122
4.3	Semiclassical Description of the Interaction Between Matter and Radiation	124

4.3.1	Quantum Description of the Matter.	124
4.3.2	Semiclassical Description of the Interaction.	125
4.3.3	Absorption Coefficient in the Semiclassical Approach.	125
4.3.4	The Scattering in the Semi-classical Approach.	127
4.4	Quantum Description of the Absorption and Scattering.	130
4.4.1	Quantum Description of the Electromagnetic Field.	130
4.4.2	Quantum Description of the Interaction of Electromagnetic Fields and Matter	131
4.4.3	Absorption Cross Section	132
4.4.4	First Order Scattering	132
4.4.5	Second Order Scattering: Anomalous and Resonant Scattering	135
4.4.6	High Energy Behaviour of the Second Order Scattering	137
4.5	Relativistic Scattering	137
4.5.1	First Order Relativistic Contribution to the Scattering	138
4.5.2	Second Order Relativistic Scattering.	139
4.5.3	Total Scattering Cross Section at High Energy.	140
References		143

5 Quantum Description of the Matter-Radiation Interaction 145

Carlo Maria Bertoni

5.1	The Classical Description of the Free Electromagnetic Field	145
5.2	The Quantized Free Electromagnetic Field	148
5.3	Moving Charges in Interaction with the Electromagnetic Field	153
5.4	The Expansion of the Amplitude of Transition.	155
5.5	Elementary Processes	157
5.6	The Matrix Element	158
5.7	Beyond the Dipole Approximation	160
5.8	Absorption.	161
5.9	Photoemission	163
5.10	Thomson Scattering	170
5.11	Second Order Processes.	171
5.12	Resonant Raman Scattering	172
5.13	Conclusions	174
5.14	Appendix.	174
References		177

Part III Experimental Methods

6	Introduction to X-Ray Absorption Spectroscopy	181
	Paolo Fornasini	
6.1	A Phenomenological Introduction to XAFS	181
6.2	Photoelectric Absorption of X-Rays	184
6.2.1	Golden Rule and Further Approximations	185
6.2.2	De-excitation Mechanisms	187
6.3	Basic EXAFS Theory	188
6.3.1	The EXAFS Function	188
6.3.2	Approximate Derivation of EXAFS	190
6.3.3	Disorder Effects on EXAFS	194
6.3.4	Summary	197
6.4	Interpretation of EXAFS Parameters	197
6.4.1	EXAFS Distance and Crystallographic Distance	198
6.4.2	Parallel and Perpendicular MSRDs	199
6.4.3	Structural Disorder	201
6.5	Experimental Techniques	201
6.5.1	Optical Apparatus	202
6.5.2	Measurement Apparatus	203
6.6	EXAFS Analysis	205
6.6.1	Extraction of the EXAFS signal	205
6.6.2	Fourier Transform and Back-Transform	207
6.6.3	Quantitative Determination of Structural Parameters	209
	References	210
7	A Close Look into the Low Energy Region of the XAS Spectra: The XANES Region	213
	Maurizio Benfatto and Carlo Meneghini	
7.1	Introduction	213
7.2	The Origin of Near Edge Features	215
7.3	Semi-quantitative Understanding of XANES Features	218
7.4	Theoretical Background and the Fit of the XANES Energy Region	220
7.5	Conclusions	237
	References	238
8	X-Ray Diffraction by Crystalline Materials	241
	Davide Viterbo and Giuseppe Zanotti	
8.1	Introduction	241
8.1.1	The Crystal	242
8.1.2	Crystal Symmetries	243

8.1.3	The X-Rays	245
8.1.4	Some Useful Mathematical Concepts	245
8.2	X-Ray Diffraction.	252
8.2.1	X-Ray Scattering	253
8.2.2	Interference of Scattered Waves	255
8.2.3	Scattering by Matter	256
8.2.4	Diffraction by a Crystal.	257
8.2.5	Other Useful Relations and Concepts	261
8.3	The Phase Problem.	263
8.3.1	Patterson Methods	264
8.3.2	Direct Methods	265
8.3.3	Other Methods Used to Solve the Phase Problem.	265
8.4	Refinement of the Crystal Structure	266
8.5	Diffraction by Polycrystalline Samples	267
8.5.1	Experimental Techniques for Obtaining Powder Diffraction Patterns.	268
8.5.2	Analysis of Powder Diffraction Patterns	271
	References	272
9	Photoemission Spectroscopy: Fundamental Aspects	275
	Carlo Mariani and Giovanni Stefani	
9.1	Introduction	275
9.2	Basic Concepts.	276
9.3	Energy Conservation, Binding Energy and Photoelectron Energy	278
9.4	Satellite Structures	281
9.4.1	Spin-Orbit Splitting.	284
9.4.2	Multiplet Splitting	284
9.4.3	Chemical Shift.	286
9.5	Molecular Photoelectron Spectroscopy	287
9.5.1	Vibrational Overtones	287
9.6	Photoelectron Angular Distributions	291
9.7	Core Hole State Relaxation	294
9.7.1	The Auger Decay	295
9.7.2	Resonant Auger and Photoemission	298
9.8	Photoemission from Solids: The Three-Step Model	300
9.9	Spectral Function of Interacting Electrons in a Solid	303
9.10	Energy Distribution Curves	305
9.10.1	Valence Band Examples (Cross-Section Exploitation and Cooper Minima).	305
9.10.2	Core Level Examples	307
9.11	Angular Resolved PhotoElectron Spectroscopy.	309
9.11.1	Band Structures	309
9.11.2	Adsorbates.	309

9.11.3	Graphite and Graphene as Exemplary 2D System	311
9.12	Final Considerations and Perspectives	314
	References	315
10	Powder Diffraction and Synchrotron Radiation	319
	Gilberto Artioli	
10.1	Powder Diffraction	319
10.2	Flat Plate Sample (Bragg-Brentano Geometry)	322
10.3	Cylindrical Sample (Debye Geometry)	324
10.4	The Implementation of Capillary Geometry at Synchrotron Sources, Case Examples	325
10.5	Basics of Instrumental Strategies	327
10.6	Time Resolved Experiments, Kinetics, Non-ambient Conditions	328
10.7	Simultaneous and Combined Studies	331
	References	333
11	Small Angle X-Ray Scattering (SAXS) with Synchrotron Radiation Sources	337
	Stefano Polizzi and Francesco Spinozzi	
11.1	The Physical Phenomenon	337
11.1.1	Why Small Angles?	338
11.1.2	How Small Is “Small”?	338
11.1.3	What Is an “Object” for SAXS?	339
11.2	Data Analysis	343
11.2.1	Guinier’s Approximation	344
11.2.2	Porod’s Law	345
11.2.3	The Scattering Power	346
11.2.4	Debye’s Approximation and Kratky Plot	347
11.2.5	Distance Distribution Function	347
11.2.6	Fractality	348
11.3	Experimental	349
11.4	Case Studies	351
	References	358
12	Resonant and Magnetic X-Ray Diffraction	361
	Luigi Paolasini	
12.1	Introduction	361
12.1.1	Theoretical Aspects of Magnetic and Resonant X-Ray Scattering	362
12.1.2	X-Rays Scattering Amplitudes	363
12.2	Experimental Methods	366
12.2.1	Polarization Analysis and Azimuthal Scans	366
12.2.2	Circular Polarisation	367

12.3	Magnetic Diffraction	369
12.3.1	Linear Polarisation Analysis of a Simple Antiferromagnetic Structure	370
12.3.2	Exemple II: Circular Polarisation Analysis in Multiferroics	372
12.4	Resonant X-Rays Scattering	375
12.4.1	Interplay Between Magnetic and Orbital Ordering in KCuF_3	378
12.4.2	High Order Multipoles in V_2O_3	380
12.5	Conclusions	383
	References	384
13	Hard X-Ray Synchrotron Imaging Techniques and Applications	389
	Jean-Yves Buffiere and José Baruchel	
13.1	Introduction	389
13.2	Imaging Techniques	391
13.2.1	Absorption Radiography	391
13.2.2	Microtomography	393
13.2.3	Phase Imaging	394
13.2.4	Microbeam Based X-Ray Imaging Techniques/Nano Imaging	398
13.2.5	X-Ray Bragg Diffraction Imaging	400
13.3	Selected Examples of the Application of Synchrotron Radiation Imaging Techniques	403
13.4	Conclusion	406
	References	407
14	X-Ray Microscopy	409
	Diane Eichert	
14.1	Introduction	409
14.2	Fundamentals of X-Ray Microscopy	411
14.2.1	X-Ray Sources	411
14.2.2	X-Ray Optics	412
14.2.3	Detectors	412
14.3	Imaging Modes	413
14.3.1	Interactions of X-Rays with Matter	413
14.3.2	Contrast Mechanisms	414
14.4	Imaging Methods	417
14.4.1	Projection Microscopy	418
14.4.2	Transmission X-Ray Microscope	419
14.4.3	Scanning Transmission X-Ray Microscope	420
14.4.4	Complementary Techniques and Methodological Developments	421

14.5	Experimental Conditions	423
14.5.1	Experimental Conditions	424
14.5.2	Conditions of Analysis	424
14.6	Applications.	426
14.6.1	Materials Science	427
14.6.2	Environmental Science	428
14.6.3	Life Science.	429
14.7	Conclusions	431
	References	432
15	Infrared Synchrotron Radiation: From the Production to the Scientific Applications.	437
	Andrea Perucchi, Lisa Vaccari and Stefano Lupi	
15.1	Introduction	437
15.2	IRSR Figures of Merits	438
15.2.1	Definitions.	438
15.2.2	Emitted Power	441
15.2.3	Brilliance.	442
15.3	Unconventional SR Sources.	444
15.3.1	Edge Radiation.	444
15.3.2	Superradiance Phenomena and Terahertz Coherent Radiation	445
15.4	Application of IRSR	446
15.4.1	Applications of IRSR at High Pressure	446
15.4.2	Terahertz Spectroscopy	450
15.4.3	Synchrotron Radiation Infrared Microspectroscopy for Biology and Medicine	452
15.4.4	Synchrotron Radiation Infrared Microspectroscopy for Cultural Heritage.	457
	References	458
16	The High-Frequency Atomic Dynamics of Disordered Systems Studied by High-Resolution Inelastic X-Ray Scattering	461
	Giulio Monaco	
16.1	Introduction	461
16.2	The High-Resolution Inelastic X-Ray Scattering Experiment	464
16.3	Models to Describe the IXS Spectra	466
16.4	Selected Results	470
16.4.1	High-Frequency Sound Waves in Glasses	470
16.4.2	Relaxation Processes in Liquids	474
16.4.3	The Non-Ergodicity Factor	477
16.5	Conclusions	480
	References	480

Part IV Applications

17 Applications of XAFS to Nanostructures and Materials Science . .	485
Federico Boscherini	
17.1 XAFS in Materials and Nanoscience.	485
17.2 Dopants.	486
17.2.1 Arsenic Dopants in Silicon Ultra-Shallow Junctions.	486
17.2.2 Solar Grade Silicon.	487
17.2.3 Silicon in Gallium Arsenide.	489
17.3 Defect Complexes	490
17.4 Bulk and Heterostructure Semiconductor Alloys.	491
17.5 Phase Transitions	492
17.6 Correlated Oxides.	494
17.7 Thin Films.	495
17.8 Semiconductor Dots	496
17.9 Metallic Clusters	497
References	497
18 Diffraction from Nanocrystalline Materials	499
Paolo Scardi and Luca Gelisio	
18.1 Introduction	499
18.2 From Single Crystal to Powder Diffraction	501
18.3 Powder Diffraction Line Profiles	503
18.4 Atomistic Modeling of Powder Diffraction from Nanocrystals	511
18.5 Conclusions	516
References	517
19 High-Energy Resolution Core Level Photoelectron Spectroscopy and Diffraction: Powerful Tools to Probe Physical and Chemical Properties of Solid Surfaces	519
Alessandro Baraldi	
19.1 Introduction	519
19.2 Single-Element Clean Metal Surfaces	521
19.2.1 Surface Core Level Shifts	521
19.2.2 Surface Reconstruction	523
19.2.3 From Surface Structure to Chemical Identity	525
19.3 Atoms and Molecules on Solid Surfaces	526
19.3.1 Adsorption and Co-Adsorption: The Adsorbate Core-Levels	526
19.3.2 Adsorption on Stepped Surfaces.	529
19.3.3 Vibrational Excitations in Chemisorbed Molecules	530
19.3.4 Adsorbate-Induced Surface Core Level Shifts	531

19.4	New Opportunities for Core Level Photoelectron Spectroscopy from Epitaxial Graphene	534
	References	537
20	Spin Polarization of the Photoelectrons and Photon Polarization of X-Ray Absorption: Spectroscopy and Magnetometry	539
	Giorgio Rossi	
20.1	Introduction	539
20.2	Definition and Measure of the Spin Polarization of the Photoelectrons	541
	20.2.1 Detecting the Electron Spin	542
	20.2.2 LS Mott Scattering	543
	20.2.3 Exchange Scattering	546
20.3	Towards the Complete Electron Spectroscopy	547
	20.3.1 Spin Polarized ARPES	547
	20.3.2 Spin Polarization of the Quantum Yield	548
	20.3.3 Matrix Element Effects	550
	20.3.4 Core Levels	550
	20.3.5 Band States	553
20.4	Symmetry Breaking Mechanisms	556
20.5	Time Resolved Experiments and High Excitation Density	559
20.6	X-Ray Absorption Dichroism	559
	20.6.1 The XMCD as Diagnostic of Magnetization	562
	20.6.2 The XMCD as a Magnetometer	564
	20.6.3 The XLD	567
	20.6.4 The X-Ray Measurement of Ferromagnetic Resonance	568
20.7	Conclusions	569
	References	569
21	Chemical and Magnetic Imaging with X-Ray Photoemission Electron Microscopy	571
	Andrea Locatelli and Tevfik Onur Mentes	
21.1	Introduction	571
21.2	Photoemission Electron Microscopy	572
	21.2.1 Instrumental Aspects	573
	21.2.2 Combination with Low Energy Electron Microscopy	575
	21.2.3 PEEM Methods	576
21.3	Applications and Examples	578
	21.3.1 Chemical Imaging of Nano-Structured Surfaces and Interfaces	578
	21.3.2 Graphene	580

21.3.3	Biominerals	581
21.3.4	Magnetic Imaging	584
21.4	Conclusions and Outlook	587
	References	588
22	Medical Imaging with Synchrotron Radiation	593
	Giuliana Tromba	
22.1	Introduction	593
22.2	Advantages of Synchrotron Radiation for Medical Imaging	594
22.3	Current Research Status at SR Beamlines	595
22.3.1	Angiography	595
22.3.2	Microangiography	596
22.3.3	Bronchography	597
22.3.4	Breast Imaging	597
22.3.5	Imaging of Cartilages	601
22.3.6	Lungs Imaging	603
22.3.7	Microvascularization and Imaging of Soft Tissues	606
22.3.8	Brain Imaging	608
22.4	Conclusions	609
	References	611
23	Synchrotron Radiation and Bio-crystallography	615
	Marco Nardini and Martino Bolognesi	
23.1	Macromolecular Crystals	615
23.1.1	Physical and Chemical Properties	616
23.1.2	Crystal Growth	616
23.1.3	Crystal Handling and Radiation Damage	618
23.2	X-Ray Diffraction and Phasing Problem	620
23.2.1	Fundamentals of Crystallography	620
23.2.2	Solution of the Phase Problem	623
23.2.3	The MIR Method	624
23.2.4	The SIRAS Method	626
23.2.5	The MAD Method	628
23.2.6	The Molecular Replacement Method	629
23.3	Density Modification	631
23.4	Crystallographic Refinement	632
23.4.1	Least Squares Refinement	632
23.4.2	Maximum-Likelihood Refinement	634
23.4.3	Quality of the Model	636
23.5	The Protein Data Bank	637
23.6	Structural Genomics	638
	References	639

24	Synchrotron Radiation in the Earth Sciences	641
	Simona Quartieri	
24.1	Introduction	641
24.2	X-Ray Diffraction	644
24.2.1	X-Ray Powder Diffraction	644
24.2.2	Single-Crystal X-Ray Diffraction	644
24.3	X-Ray Absorption Spectroscopy	646
24.4	X-Ray Fluorescence Microanalysis	648
24.5	Materials Under Extreme Conditions	649
24.5.1	Single-Crystal and Powder X-Ray Diffraction	653
24.5.2	Single-Crystal and Powder IR Spectroscopy	653
24.5.3	X-Ray Absorption Spectroscopy	654
24.5.4	HP Synchrotron Mössbauer	655
24.6	X-Ray Tomography and Topography	655
24.7	Future Prospects	656
	References	656
25	Synchrotron Radiation and Environmental Sciences	661
	Giovanni De Giudici, Piero Lattanzi and Daniela Medas	
25.1	Introduction: What Is Environmental Science?	661
25.2	Overview of the Most Common Techniques	663
25.2.1	Synchrotron-Based X-Ray Diffraction	664
25.2.2	X-Ray Absorption Spectroscopy	664
25.2.3	Microbeam Techniques	666
25.2.4	Surface Techniques	669
25.3	Case History: Zinc Biomineralization at Narcauli, Sardinia	671
25.4	Concluding Remarks	673
	References	674
26	Synchrotron Radiation in Art, Archaeology and Cultural Heritage	677
	Simona Quartieri	
26.1	Introduction	677
26.2	Examples of SR-X-Ray Diffraction Studies of Cultural Heritage	678
26.3	Archaeometric Applications of X-Ray Absorption Spectroscopy	682
26.4	SR-Based FT-Infrared Micro-Spectroscopy Applied to Cultural Heritage	688
26.5	SR-Based Techniques for Non-Destructive Sub-surface Analysis of Painted Cultural Heritage Artifacts	688
26.6	X-Ray Computed Tomography in Cultural Heritage Studies	689

26.7	Application of SR-Based Techniques to the Study of Paleontological Findings	691
26.8	Recent and Future Trends	693
	References	693
27	Synchrotron Radiation and Chemistry: Studies of Materials for Renewable Energy Sources	697
	Antonino Martorana, Francesco Giannici and Alessandro Longo	
27.1	Introduction	697
27.2	Metal-Organic Frameworks	699
27.3	Hydrides for Hydrogen Storage	701
27.4	Dye-Sensitized Solar Cells.	704
27.5	Oxide-Ion and Proton Conductors.	706
27.6	Electrodes for Fuel Cells.	710
27.7	Conclusions	713
	References	713
28	Catalyst Characterization by XAS and XES Spectroscopies: In Situ and Operando Experiments.	717
	Francesca Bonino, Elena Groppo, Carmelo Prestipino, Giovanni Agostini, Andrea Piovano, Diego Gianolio, Lorenzo Mino, Erik Gallo and Carlo Lamberti	
28.1	Introduction	718
28.2	Methods and Instrumentation	719
28.3	Understanding the Structure of the Ti Active Site in TS-1 Catalyst: A XAS/XES Study	721
28.4	Understanding the Chemistry of the Oxychlorination Catalysis by In Situ and Operando Experiments.	727
28.5	Conclusions and Perspectives.	731
	References	733
29	Studies of Matter at Extreme Conditions.	737
	Sakura Pascarelli	
29.1	High Pressure Research.	737
29.1.1	Introduction	738
29.1.2	Matter Under "Extreme Conditions"	738
29.1.3	High Pressure to Study Earth's Interior, Understand Climate Change, Explore New Sources of Energy . . .	739
29.1.4	Tools and Experimental Methods	741
29.2	Physics	744
29.2.1	Collapse of Ferromagnetism in the 3d Metals	744
29.2.2	Examples of Recent Work on Fe, Co and Ni	746

29.3	Earth Science	750
29.3.1	Fe Partitioning in the Earth Mantle.	750
29.3.2	Fe Partitioning at and Beyond the Core-Mantle Boundary.	753
29.4	Energy, Environment, Climate	755
29.4.1	The Deep Carbon Cycle	755
29.4.2	Stability of Hydrocarbons in the Deep Earth	756
29.4.3	Exploring the Nature of C-bearing Minerals	757
	References	759
30	Science Frontiers with X-Ray Free Electron Laser Sources	761
	Flavio Capotondi, Martina Dell'Angela, Marco Malvestuto and Fulvio Parmigiani	
30.1	Introduction	762
30.2	Coherent Free Electron Laser Sources.	763
30.3	Coherent Diffraction Imaging with Free Electron Lasers.	765
30.4	Spectroscopy on Solids at FELs	768
30.4.1	Photoelectron Spectroscopy	770
30.4.2	X-Ray Absorption Spectroscopy.	773
30.4.3	Resonant X-Ray Emission Spectroscopy	774
30.5	Magneto-Dynamical Studies.	778
30.5.1	Ultra Fast X-Ray Experiments	781
30.5.2	Ferromagnetism and Superconductivity: A Background Starting Point	782
30.5.3	Physics of FM/SC Heterostructures.	783
30.5.4	New and Promising Fields of Research and Innovation	783
	References	784
	Index	787