

TABLE OF CONTENTS

Contributors.....	XV
Foreword.....	XIX
Introduction.....	XXI

X-RAY SPECTROSCOPY

1 - Fundamentals of X-ray absorption and dichroism: the multiplet approach	
F. de Groot - J. Vogel.....	3
1. Introduction.....	4
1.1. Interaction of X-rays with matter.....	4
1.2. Basics of XAFS spectroscopy.....	6
1.3. Experimental aspects.....	9
2. Multiplet effects.....	11
2.1. Atomic multiplets.....	14
2.1.1. Term symbols.....	14
2.1.2. Matrix elements.....	18
2.2. Atomic multiplet ground states of $3d^n$ systems.....	20
2.3. j - j coupling.....	20
2.4. X-ray absorption spectra described with atomic multiplets.....	21
2.4.1. Transition metal L_{II-III} edge.....	21
2.4.2. M_{IV-V} edges of rare earths.....	28
3. Crystal field theory.....	31
3.1. The crystal field multiplet Hamiltonian.....	32
3.2. Cubic crystal fields.....	33
3.3. The energies of the $3d^n$ configurations.....	35
3.3.1. Symmetry effects in D_{4h} symmetry.....	40
3.3.2. The effect of the $3d$ spin-orbit coupling.....	40
3.3.3. The effects on the X-ray absorption calculations.....	42
3.3.4. $3d^0$ systems in octahedral symmetry.....	43
3.3.5. $3d^0$ systems in lower symmetries.....	45
3.3.6. X-ray absorption spectra of $3d^n$ systems.....	46
4. Charge transfer effects.....	47
4.1. Initial state effects.....	47
4.2. Final state effects.....	52
4.3. The X-ray absorption spectrum with charge transfer effects.....	53
5. X-ray linear and circular dichroism.....	59
References.....	64

2 - Multiple scattering theory applied to X-ray absorption near-edge structure	
P. Sainctavit - V. Briois - D. Cabaret	67
1. Introduction	67
2. MST for real space calculations	70
2.1. The absorption cross-section	71
2.2. Calculation of the cross-section for three different potentials	73
2.2.1. Free particle	73
2.2.2. Particle in a spherical potential	75
2.2.3. Particle in a "muffin-tin" potential	78
3. Construction of the potential	83
3.1. X - α exchange potential	85
3.2. Dirac-Hara exchange potential	85
3.3. Complex Hedin-Lundqvist exchange and correlation potential	87
4. Application of the multiple scattering theory	89
4.1. Vanadium K edge cross-section for VO ₆ cluster	90
4.2. Iron K edge cross-section for FeO ₆ cluster	93
4.3. Cross-section calculations in distorted octahedra	94
5. Spin transition in Fe ^{II} (o-phenantroline) ₂ (NCS) ₂ followed at the iron K edge	95
6. Conclusion	97
Appendix - Expression for the propagators J_{LL}^{11} and H_{LL}^{11}	97
Acknowledgments	99
References	100
3 - X-ray magnetic circular dichroism	
F. Baudelet	103
1. Introduction	103
2. Origins of magnetic circular dichroism	104
2.1. Theoretical aspects: role of the spin-orbit coupling	104
2.2. Light polarization and polarization-dependent selection rules	106
2.3. Origin of the XMCD signal	108
2.3.1. Heuristic model: L _{II} - L _{III} edges of transition metals and rare earth elements	108
2.3.2. Calculation of P _e for the L _{II} - L _{III} edges: P _e (L _{II}) and P _e (L _{III})	109
2.3.3. Calculation of P _e for the K - L _I edges: P _e (K) and P _e (L _I)	112
2.4. Magnitude of the XMCD signal	113
3. The sum rules	114
4. XMCD signal at the K edges (1s → p)	117
5. XMCD and localized magnetism (multiplet approach)	118
6. L _{II} - L _{III} edges of rare earths	121
7. Magnetic EXAFS	125
8. Application to multilayers with GMR	126
9. Study of highly correlated [Ce/La/Fe] and [La/Ce/Fe] multilayers	127
References	128

4 - Extended X-ray absorption fine structure	
B. Lengeler	131
1. Introduction	131
2. X-ray absorption in isolated atoms	133
3. X-ray absorption fine structure (XAFS).....	136
3.1. X-ray absorption fine structure: the basic formula	136
3.2. Corrections to the basic EXAFS formula.....	141
3.2.1. Spherical photoelectron wave.....	142
3.2.2. Multiple scattering	142
3.3. Set-up for measuring X-ray absorption.....	143
3.4. XAFS data analysis.....	145
3.5. Position and structure of the absorption edge	149
4. Some applications of XAS.....	153
4.1. Lattice distortion around impurities in dilute alloys.....	154
4.2. Precipitation in immiscible giant magnetoresistance $Ag_{1-x}Ni_x$ alloys.....	155
4.3. Lattice site location of very light elements in metals by XAFS.....	158
4.4. Valence of iridium in anodically oxidized iridium films	160
4.5. Copper-based methanol synthesis catalyst.....	163
4.6. Combined X-ray absorption and X-ray crystallography	165
References	167
5 - Inelastic X-ray scattering from collective atom dynamics	
F. Sette - M. Krisch.....	169
1. Introduction	169
2. Scattering kinematics and inelastic X-ray scattering cross-section.....	170
3. Experimental apparatus.....	175
4. The "fast sound" phenomenon in liquid water.....	179
5. Determination of the longitudinal sound velocity in iron to 110 GPa.....	182
6. Conclusions and outlook.....	186
References	187
6 - Photoelectron spectroscopy	
M. Grioni	189
1. Introduction	189
2. What is photoemission?	190
3. Photoemission in the single-particle limit - Band mapping	193
4. Beyond the single-particle approximation	201
5. Case studies	209
5.1. Fermi liquid lineshape in a normal metal.....	209
5.2. Gap spectroscopy	215
5.3. Electronic instabilities in low dimensions.....	220
5.4. Some recent developments	229
6. Conclusions	235
References	236

7 - Anomalous scattering and diffraction anomalous fine structure	
J.L. Hodeau - H. Renevier	239
1. Anomalous scattering, absorption and refraction	240
2. Theoretical versus experimental determination of anomalous contribution	241
3. Applications of anomalous dispersion	244
3.1. Structure factor phase solution (MAD method).....	245
3.2. Element-selective diffraction (contrast method).....	247
4. Diffraction anomalous fine structure data analysis.....	249
4.1. DAFS and EDAFS formalism	251
4.1.1. Single anomalous site analysis	252
4.1.2. Multiple anomalous site analysis	253
4.2. DAFS and EDAFS determination	255
4.3. DAFS and DANES valence determination	258
4.4. Anisotropy of anomalous scattering.....	260
5. Requirements for anomalous diffraction experiments.....	262
6. Conclusion.....	263
References	264
8 - Soft X-ray photoelectron emission microscopy (X-PEEM)	
C.M. Schneider	271
1. A "nanoscale" introduction	271
2. Visualizing micro- and nanostructures.....	271
3. Technical aspects of an Electron Emission Microscope (EEM)	273
3.1. Electron-optical considerations	273
3.2. Transmission and lateral resolution.....	275
4. Non-magnetic image contrast in X-PEEM.....	276
4.1. Primary contrast mechanisms	276
4.1.1. Work function contrast	276
4.1.2. Chemical contrast.....	277
4.2. Secondary contrast mechanisms.....	280
5. Magnetic contrast in X-PEEM.....	281
5.1. Magnetic X-ray Circular Dichroism (XMCD)	282
5.1.1. Physics of the magnetic contrast mechanism.....	282
5.1.2. Contrast enhancement.....	284
5.1.3. Angular dependence of the image contrast.....	285
5.1.4. Magnetic domain walls.....	286
5.1.5. Information depth.....	288
5.2. X-ray Magnetic Linear Dichroism (XMLD)	290
5.2.1. Properties of the contrast mechanism.....	290
5.2.2. Imaging domains in antiferromagnets.....	291
6. Concluding remarks	292
References	293

9 - X-ray intensity fluctuation spectroscopy	
M. Sutton	297
1. Introduction	297
2. Mutual coherence functions	301
3. Diffraction by partially coherent sources	304
4. Kinetics of materials	308
5. X-ray intensity fluctuation spectroscopy	310
6. Conclusions	316
References	317
10 - Vibrational spectroscopy at surfaces and interfaces using synchrotron sources and free electron lasers	
A. Tadjeddine - P. Dumas	319
1. Introduction	319
2. Infrared synchrotron source and free electron lasers	321
2.1. Infrared synchrotron sources	321
2.1.1. Principles	321
2.1.2. Extraction of the IR beam from the synchrotron ring	324
2.1.3. Fourier transform interferometer	324
2.2. Non linear surface spectroscopy with conventional and free electron lasers	325
2.2.1. Principle of SFG	326
2.2.2. Experimental SFG set-up	328
2.2.3. The CLIO-FEL infrared laser	328
3. Examples of applications in Surface Science	331
3.1. Synchrotron infrared spectroscopy at surfaces	331
3.1.1. Low frequency modes of adsorbed molecules and atoms	333
3.1.2. Vibrational dynamics of low frequency modes	335
3.2. Sum Frequency and Difference Frequency Generation at interfaces	339
3.2.1. Identification of adsorbed intermediate of electrochemical reactions by SFG	340
3.2.2. Vibrational spectroscopy of cyanide at metal-electrolyte interface	342
3.2.3. Vibrational spectroscopy of self-assembled monolayers on metal substrate	346
3.2.4. Vibrational spectroscopy of fullerenes C ₆₀ , adsorbed on Ag(111), in UHV environment	348
3.2.5. Adsorption of 4-cyanopyridine on Au(111) monitored by SFG	352
4. Conclusion and outlook	356
References	356

NEUTRON SPECTROSCOPY

11 - Inelastic neutron scattering: introduction	
R. Scherm - B. Fåk	361
1. Interaction of neutrons with matter	361
2. Kinematics	362
2.1. Energy and momentum conservation	362
2.2. Scattering triangle	363
2.3. Parabolas	364
3. Master equation and $S(Q, \omega)$	364
4. Correlation function	366
5. Coherent and incoherent scattering	367
6. General properties of $S(Q, \omega)$	369
6.1. Detailed balance	369
6.2. Moments	370
6.3. Total versus elastic scattering	371
7. Magnetic scattering	372
8. Response from simple systems	373
8.1. Examples	373
8.2. Response functions	375
9. Instrumentation	376
9.1. TAS	378
9.2. TOF	379
10. How to beat statistics	379
References	380
12 - Three-axis inelastic neutron scattering	
R. Currat	383
1. Principle of the technique	383
2. The three-axis spectrometer	386
3. The TOF versus TAS choice	391
4. What determines the TAS count rate?	394
5. What determines the size and shape of the resolution function?	396
6. Decoupling energy and momentum resolutions: direct space focusing	400
7. TAS multiplexing	403
8. Phonon studies with TAS	408
9. The INS versus IXS choice	412
10. Magnetic excitation studies with TAS	415
11. Practical aspects	420
12. Summary and outlook	422
References	423

13 - Neutron spin echo spectroscopy	
R. Cywinski.....	427
1. Introduction	427
2. Polarized neutron beams, Larmor precession and spin flippers	428
3. Generalized neutron spin echo	432
4. Polarization dependent scattering processes	436
5. Practicalities: measurement of the spin echo signal	440
6. Applications of neutron spin echo spectroscopy	444
6.1. Soft condensed matter.....	444
6.2. Glassy dynamics	447
6.3. Spin relaxation in magnetic systems	449
7. Conclusions	453
Bibliography	453
References	454
14 - Time-of-flight inelastic scattering	
R. Eccleston	457
1. Introduction	457
2. Classes of TOF spectrometers	458
2.1. Distance-time plots	458
2.2. Kinematic range	460
3. Beamline components	461
3.1. Choppers.....	461
3.1.1. Fermi choppers.....	462
3.1.2. Disk choppers.....	462
3.1.4. T = 0 choppers.....	462
3.2. Monochromating and analyzing crystals	463
3.3. Filters.....	463
3.4. Detectors.....	464
3.5. Neutron guides	464
3.6. Polarizers and polarization analysis	465
4. Direct geometry spectrometers	465
4.1. Chopper spectrometer on a pulsed source.....	465
4.2. Chopper spectrometers on a steady state source.....	466
4.3. Multi-chopper TOF spectrometers	467
5. Resolution and spectrometer optimization	469
6. Flux	470
7. Resolution as a function of energy transfer and experimental considerations	471
Single crystal experiments on a chopper spectrometer.....	472
8. Indirect geometry spectrometers	474
8.1. The resolution of indirect geometry spectrometers	475
8.2. Backscattering spectrometer.....	475
8.3. Crystal analyser spectrometers.....	477

8.4. Deep inelastic neutron scattering.....	478
8.5. Coherent excitations.....	479
9. Conclusions	480
Further information	481
References	481
15 - Neutron backscattering spectroscopy	
B. Frick	483
1. Introduction	483
2. Reflection from perfect crystals and its energy resolution	485
3. Generic backscattering spectrometer concepts	488
3.1. Neutron optics of the primary spectrometers of reactor-BS instruments.....	489
3.2. Neutron optics of the primary spectrometer of spallation source-BS instruments...	493
3.3. Secondary spectrometer.....	493
4. Total energy resolution of the spectrometers	494
5. How to do spectroscopy?	494
5.1. Spectroscopy on reactor based instruments	494
5.2. Spectroscopy on spallation source-BS instruments.....	497
6. More details on optical components	498
6.1. BS monochromators and analysers	498
6.2. How to obtain the best energy resolution in backscattering?.....	499
6.3. Mosaic crystal deflectors and Phase Space Transformer	500
6.4. Neutron guides	503
6.5. Higher order suppression.....	503
6.6. Q-resolution.....	504
6.7. A second time through the sample?	504
7. Examples for backscattering instruments	505
7.1. Reactor instruments	505
7.2. Spallation source instruments.....	509
8. Data treatment	511
9. Typical measuring methods and examples	513
9.1. Fixed window scans.....	513
9.2. Spectroscopy	516
References	525
16 - Neutron inelastic scattering and molecular modelling	
M.R. Johnson - G.J. Kearley - H.P. Trommsdorff	529
1. Introduction	529
2. Theory framework for tunnelling, vibrations and total energy calculations	532
2.1. Hamiltonians for quantum tunnelling	532
2.2. The dynamical matrix for molecular vibrations.....	536
2.3. Total energy calculations for determining PES and force constants	538
3. Experimental techniques for measuring rotational tunnelling and molecular vibrations	540

4. Numerical simulations for understanding INS spectra	544
4.1. SPM methyl group tunnelling.....	544
4.2. Multi-dimensional tunnelling dynamics of methyl groups	546
4.3. Vibrational spectroscopy of molecular crystals.....	547
5. Discussion	551
References	553
Index	557