

Core Level Spectroscopy of Solids

Frank de Groot
Akio Kotani



CRC Press
Taylor & Francis Group

Core Level Spectroscopy of Solids

Frank de Groot
Akio Kotani



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **Informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2008 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-0-8493-9071-5 (Hardcover)

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

No part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC) 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Groot, Frank de, 1964-

Core level spectroscopy of solids / Frank de Groot and Akio Kotani.

p. cm. -- (Advances in condensed matter science ; v. 6)

Includes bibliographical references and index.

ISBN 978-0-8493-9071-5 (alk. paper)

1. Solids--Spectra. 2. Spectrum analysis. 3. Electron spectroscopy. 4.

Energy-band theory of solids. I. Kotani, A. (Akio), 1941- II. Title. III. Series.

QC176.8.O6G76 2008

530.4'16--dc22

2007029414

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Advances in Condensed Matter Science

Edited by D.D. Sarma, G. Kotliar and Y. Tokura

Volume 1

Strong Coulomb Correlations in Electronic Structure Calculations:
Beyond the Local Density Approximation

Edited by Vladimir I. Anisimov

Volume 2

Colossal Magnetoresistive Oxides

Edited by Yoshinori Tokura

Volume 3

Spin Dependent Transport in Magnetic Nanostructures

Edited by Sadamichi Maekawa and Teruya Shinjo

Volume 4

Electronic Structure of Alloys, Surfaces and Clusters

Edited by Abhijit Mookerjee and D.D. Sarma

Volume 5

Advances in Amorphous Semiconductors

Jai Singh and Koichi Shimakawa

Volume 6

Core Level Spectroscopy Solids

Frank de Groot and Akio Kotani

*This book is dedicated to our partners
Hedwig te Molder and Machiko.*

Preface

Core level spectroscopy is a powerful tool for the study of electronic states in solids where the precise information of valence electron states can be detected through excitation of core electrons with a local and sensitive probe. Traditionally, the study of the electronic and optical properties of solids was performed with photons in the visible and infrared region of the spectrum. Since the development of second generation synchrotron radiation sources in the 1970s, the use of x-rays has expanded widely. The most characteristic feature of an x-ray is that it excites a core electron; in other words, x-ray spectroscopy has opened a new door on core level spectroscopy. A direct implication is that the information on core level spectroscopy is local and element specific. The experimental study of core level spectroscopy has made remarkable progress using high-brilliance third-generation synchrotron radiation sources. In order to interpret new experimental data, theoretical study of core level spectroscopy has made continuous progress over the last 30 years and has made a major contribution to the physical understanding of spectroscopy.

This book examines fundamental and theoretical aspects of core level spectroscopy including x-ray photoemission spectroscopy, x-ray absorption spectroscopy, and resonant x-ray emission spectroscopy. With an emphasis on interpreting core level spectroscopy for transition metal and rare earth systems from a model based on charge transfer multiplet theory, this book presents typical experimental results and discusses various theoretical approaches such as atomic multiplet theory, ligand field theory, and charge transfer multiplet theory, making it an ideal reference for the research community.

The two authors, Frank de Groot and Akio Kotani, have been studying core level spectroscopy of solids for many years. Since the end of the 1980s, Frank de Groot has been involved in both experimental and theoretical studies on a wide range of materials. Akio Kotani has contributed to the theoretical development of this field continuously since his pioneering work in the 1970s. This book concentrates on the charge transfer multiplet theory for f and d electron systems. A wide range of other theoretical approaches are also touched upon briefly. All chapters were written jointly, although Chapters 2, 4, and 6 were mainly written by Frank de Groot and Chapters 3, 5, and 8 by Akio Kotani. It is the authors' hope that this book is useful for all researchers involved in x-ray and electron spectroscopy. This includes the users of x-ray spectroscopy and microscopy beamlines, plus all students and researchers interested in the study of core level spectroscopy.

Frank de Groot
Akio Kotani

Acknowledgments

This book is the outcome of twenty years of work in core level spectroscopy. I was thoroughly introduced to this field by an energetic John Fuggle. Theo Thole and George Sawatzky guided me in the theoretical analysis of core level spectra. I would like to thank them very much for having had the opportunity to work with them. Special thanks to Jeroen Goedkoop and Marco Grioni, who introduced me into the synchrotron world.

In addition, I would like to thank all the colleagues with whom I had the pleasure to discuss the various aspects of core level spectroscopy, to perform experiments at synchrotron radiation sources and to perform the calculations. I would like to mention John Inglesfield, Jan Vogel, Miguel Abbate, Leonardo Soriano, Francesca Lopez, Zhiwei Hu, Pieter Kuiper, Jan van Elp, Hao Tjeng, Michel van Veenendaal, Eric Pellegrin, Gerrit van der Laan, Jan Zaanen, Olle Gunnarsson, Lars Hedin, Teijo Åberg, Massimo Altarelli, Paolo Carra, Francesco Sette, CT Chen, Marie-Anne Arrio, Philippe Sainctavit, Christian Brouder, Delphine Cabaret, Alain Fontaine, Stephania Pizzini, Helio Tolentino, Cinthia Piamonteze, Steve Cramer, Pieter Glatzel, Uwe Bergmann, Xin Wang, Weiwei Gu, Simon George, Chi-chang Kao, Keijo Hämäläinen, Michael Krisch, Gyorgy Vanko, Ed Solomon, Eric Wasinger, Rosalie Hocking, Serena George de Beer, Axel Knop-Gericke, Michael Havecker, Claudia Dallera, Sergei Butorin, Jinghua Guo, Odile Stephan, Christian Colliex, John Rehr, Atsushi Fujimori, Takeo Jo, Arata Tanaka, Harohiko Ogasawara, Diek Koningsberger, Moniek Tromp, Jeroen van Bokhoven, Willem Heijboer, Ingmar Swart, and Bert Weckhuysen.

Frank de Groot

The manuscript of this book was written mainly at RIKEN/Spring-8 and PF/KEK, and I would like to thank Professor S. Shin (RIKEN) and Professors K. Nasu, T. Koide, and T. Iwazumi (PF) for their kind support and helpful discussions on core level spectroscopy. Parts of the manuscript were also prepared at ALS (Berkeley), IPCMS (Strasbourg) and LMCP (Paris), and thanks are due to Dr. Z. Hussain and Dr. J. H. Guo (ALS), Dr. J. C. Parlebas (IPCMS), and Professor A. Shukla (LMCP) for their hospitality and collaboration. In the preparation of the manuscript, two issues from a collection of papers entitled *Core Level Spectroscopy in Solids* (edited by K. Okada, S. Tanaka, T. Uozumi, and H. Ogasawara) and *Progress in Core-Level Spectroscopy of Condensed Systems* (edited by S. Shin, K. Okada, and T. Ohta) were very helpful. The two issues were edited on the occasion of my retirement from the University of Tokyo. The former is a collection of review papers written by myself and coauthors that was edited in 2003 (not for sale), and the latter is a collection of invited papers published in a special issue of *Journal of Electron Spectroscopy and Related Phenomena*, vol. 136, 2004. Special thanks are due to the editors of the two

issues for their efforts. In addition to those colleagues just mentioned, I would also like to thank Professors I. Harada, T. Jo, Y. Kayanuma, Y. Maruyama, T. Miyahara, G. A. Sawatzky, L. Braicovich, C. Hague, J. Nordgren, C.-C. Kao, D. Chandesris, A. Bianconi, and Drs M. Nakazawa, M. Taguchi, T. Idé, M. Matsubara, K. Fukui, K. Asakura, Y. Harada, T. Nakamura, B. T. Thole, L. C. Duda, S. Butorin, P. Le Fèvre, M. Calandra, and many others not mentioned here, for their help and for discussions on a variety of subjects. It is my great pleasure to express particular gratitude to the late Professors T. Nagamiya and K. Motizuki, and Professors J. Kanamori and M. Tachiki for leading me to the theoretical study of condensed matter physics. Finally, my thanks go to Professor Y. Toyozawa for leading me to one of the most significant and enjoyable research fields, namely, core level spectroscopy.

Akio Kotani

We are both grateful to D.D. Sarma (series editor), Jill Jurgensen, and many others at CRC Press who have contributed to the production of this book.

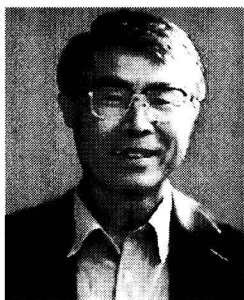
Authors



Frank de Groot is an associate professor in the department of chemistry at Utrecht University. His work reflects a concern with both the theoretical and experimental aspects of x-ray spectroscopy. His current interest is in the use of x-ray spectroscopies for the study of the electronic and magnetic structure of condensed matter, in particular for transition metal oxides, (magnetic) nanoparticles and heterogeneous catalysts under working conditions. He has taught international workshops and courses on x-ray spectroscopy at universities in Berkeley, Davis, Trieste, Grenoble, Berlin, and Zurich. Synchrotron experiments

have been performed in Orsay, Grenoble, Berlin, Hamburg, Karlsruhe, Lund, Zurich, Daresbury, Brookhaven, Stanford, Argonne, and Berkeley. He has given over 130 lectures and published more than 160 articles.

Frank de Groot studied chemistry at the University of Nijmegen where, in 1991, he received his PhD under the supervision of John Fuggle. The title of his thesis was "X-Ray Absorption Spectroscopy of Transition Metal Oxides." From 1992, he was a postdoctoral fellow at the LURE Synchrotron in Orsay, France. In 1995, he became a Royal Netherlands Academy of Arts fellow at the University of Groningen, under the supervision of George Sawatzky. He obtained a personal *vidi* grant from the Netherlands Organization for Scientific Research. In 2006, he was awarded the prestigious *vici* grant allowing him to further extend his line of research at Utrecht University.



Akio Kotani is a professor emeritus at the University of Tokyo. He received his doctorate degree from Osaka University in 1969. He worked as a research associate for three years at Osaka University and then for five years at the Institute for Solid State Physics of the University of Tokyo. As an associate professor, he spent four years at the Institute of Material Science of Tohoku University followed by six years at Osaka University. In 1987, he was appointed a full professor at Tohoku University, and moved again in 1991 to the Institute for Solid State Physics of the University of Tokyo. He retired from the University of

Tokyo in 2003, and is now a senior visiting scientist at RIKEN/Spring-8 and a collaborative scientist at KEK-Photon Factory.

Professor Kotani is well known for his many distinguished contributions to the vast area of theoretical condensed matter physics. His early works involved the

magnetic properties of the spin-density-wave in chromium metal, the electromagnetic properties in magnetic superconductors, the optical response from localized electrons coupled with a phonon field, etc. Among these extensive theoretical studies was his pioneering work on core-level spectroscopy, which was proposed in 1973 and 1974 to interpret peculiar features in core-level XAS and XPS spectra of strongly correlated electron systems. Since then, for three decades, he has worked to develop the theoretical aspect of core-level spectroscopy. He has encouraged many young researchers and experimentalists in this field, and his scientific predictions have often been guiding principles for experimentalists working with synchrotron light sources.

Contents

Preface	xv
Acknowledgments	xvii
Authors	xix
Chapter 1 Introduction	1
Chapter 2 Fundamental Aspects of Core Level Spectroscopies	11
2.1 Core Holes	11
2.1.1 Creation of Core Holes	11
2.1.2 Decay of Core Holes	12
2.2 Overview of Core Level Spectroscopies	14
2.2.1 Core Hole Spin–Orbit Splitting	14
2.2.2 Core Hole Excitation Spectroscopies	15
2.2.3 Core Hole Decay Spectroscopies	18
2.2.4 Resonant Photoelectron Processes	19
2.2.5 Resonant X-Ray Emission Channels	22
2.2.6 Overview of the RXES and NXES Transitions	23
2.3 Interaction of X-Rays with Matter	25
2.3.1 Electromagnetic Field	26
2.3.2 Transition to Quantum Mechanics	26
2.3.3 Interaction Hamiltonian	27
2.3.4 Golden Rule	27
2.4 Optical Transition Operators and X-Ray Absorption Spectra	28
2.4.1 Electric Dipole Transitions	29
2.4.2 Electric Quadrupole Transitions	29
2.4.3 Dipole Selection Rules	29
2.4.4 Transition Probabilities, Cross Sections, and Oscillator Strengths	30
2.4.5 Cross Section, Penetration Depth, and Excitation Frequency	31
2.4.6 X-Ray Attenuation Lengths	32
2.5 Interaction of Electrons with Matter	32
2.6 X-Ray Sources	34
2.6.1 Synchrotron Radiation Sources	34
2.6.2 X-Ray Beamlines and Monochromators	35
2.6.3 Other X-Ray Sources	36
2.7 Electron Sources	37

Chapter 3	Many-Body Charge-Transfer Effects in XPS and XAS	39
3.1	Introduction	39
3.2	Many-Body Charge-Transfer Effects in XPS	40
3.2.1	Basic Description of the XPS Process	40
3.3	General Expressions of Many-Body Effects	42
3.3.1	General Description	42
3.3.2	Generating Function and Dielectric Response	44
3.3.3	XPS Spectrum and Its Limiting Forms	45
3.3.3.1	Slow Modulation Limit	47
3.3.3.2	Rapid Modulation Limit	47
3.4	General Effects in XPS Spectra	47
3.4.1	Screening by Free-Electron-Like Conduction Electrons	47
3.4.2	Screening by Lattice Relaxation Effects	49
3.4.3	Shake-Up Satellites	50
3.4.4	Lifetime Effects	50
3.4.4.1	Auger Transition	50
3.4.4.2	Radiative Transition	51
3.5	Typical Examples of XPS Spectra	52
3.5.1	Simple Metals	52
3.5.2	La Metal	56
3.5.2.1	Final State of Type (A)	59
3.5.2.2	Final State of Type (B)	60
3.5.3	Mixed Valence State in Ce Intermetallic Compounds	62
3.5.4	Insulating Mixed Valence Ce Compounds	67
3.5.5	Transition Metal Compounds	71
3.5.5.1	Model	71
3.5.5.2	Simplified Analysis	72
3.5.5.3	Case A: $\Delta_f > 0$ ($\Delta > U_{dc}$)	74
3.5.5.4	Case B: $\Delta_f \leq 0$ ($\Delta \leq U_{dc}$)	74
3.6	Many-Body Charge-Transfer Effects in XAS	76
3.6.1	General Expressions of Many-Body Effects	76
3.6.2	XAS in Simple Metals	76
3.6.3	XAS in La Metal	78
3.6.3.1	Case A: $\epsilon_f < \epsilon_F$	79
3.6.3.2	Case B: $\epsilon_f > \epsilon_F$	80
3.6.4	Ce 3d XAS of Mixed Valence Ce Compounds	81
3.6.5	Ce L_3 XAS	83
3.6.6	XAS in Transition Metal Compounds	87
3.7	Comparison of XPS and XAS	89
Chapter 4	Charge Transfer Multiplet Theory	93
4.1	Introduction	93
4.2	Atomic Multiplet Theory	95
4.2.1	Term Symbols	96
4.2.2	Some Simple Coupling Schemes	98

4.2.3	Term Symbols of d-Electrons	101
4.2.4	Matrix Elements	105
4.2.5	Energy Levels of Two d-Electrons	107
4.2.6	More Than Two Electrons	108
4.2.7	Matrix Elements of the $2p^3$ Configuration	109
4.2.8	Hund's Rules	110
4.2.9	Final State Effects of Atomic Multiplets	111
4.3	Ligand Field Multiplet Theory	115
4.3.1	Ligand Field Multiplet Hamiltonian	116
4.3.2	Cubic Crystal Fields	117
4.3.3	Definitions of the Crystal Field Parameters	119
4.3.4	Energies of the $3d^n$ Configurations	120
4.3.5	Symmetry Effects in D_{4h} Symmetry	124
4.3.6	Effect of the 3d Spin–Orbit Coupling	125
4.3.7	Consequences of Reduced Symmetry	126
4.3.8	$3d^0$ Systems in Octahedral Symmetry	126
4.3.9	<i>Ab Initio</i> LFM Calculations	132
4.4	Charge Transfer Multiplet Theory	133
4.4.1	Initial State Effects	134
4.4.2	Final State Effects	137
4.4.3	XAS Spectrum with Charge-Transfer Effects	138
4.4.4	Small Charge-Transfer Satellites in 2p XAS	140
4.4.5	Large Charge-Transfer Satellites in 2p XPS	141
4.4.5.1	$3d^0$ Compounds	142
4.4.5.2	$3d^8$ Compounds	143
Chapter 5	X-Ray Photoemission Spectroscopy	145
5.1	Introduction	145
5.2	Experimental Aspects	146
5.3	XPS of TM Compounds	146
5.3.1	2p XPS	146
5.3.2	Zaanen–Sawatzky–Allen Diagram	152
5.3.3	2p XPS in Early TM Systems	154
5.3.4	Effect of Multiplet Coupling on Δ and U_{dd}	158
5.3.5	3s XPS	160
5.3.6	3p XPS	164
5.4	XPS of RE Compounds	165
5.4.1	Simplified Analysis for RE Oxides	165
5.4.2	Application of Charge-Transfer Multiplet Theory	169
5.5	Resonant Photoemission Spectroscopy	176
5.5.1	Fundamental Aspects of RPES	177
5.5.2	RPES in Ni Metal and TM Compounds	180
5.5.2.1	3p RPES in Ni Metal	180
5.5.2.2	2p RPES in TM Compounds	182
5.5.2.3	3p RPES in NiO	185

5.5.3	3d and 4d RPES of Ce Compounds	185
5.5.4	Resonant XPS	187
5.5.5	Resonant Auger Electron Spectroscopy	188
5.5.6	Reducing the Lifetime Broadening in XAS	191
5.5.7	EQ and ED Excitations in the Pre-Edge of Ti 1s XAS of TiO ₂	191
5.6	Hard X-Ray Photoemission Spectroscopy	197
5.6.1	2p HAXPS of Cuprates	197
5.6.2	2p HAXPS of V ₂ O ₃ and La _{1-x} Sr _x MnO ₃	198
5.6.3	Ce Compounds: Surface/Bulk Sensitivity	199
5.6.4	Resonant HAXPS of Ce Compounds	202
5.7	Resonant Inverse Photoemission Spectroscopy	205
5.8	Nonlocal Screening Effect in XPS	212
5.9	Auger Photoemission Coincidence Spectroscopy	218
5.10	Spin-Polarization and Magnetic Dichroism in XPS	221
5.10.1	Spin-Polarized Photoemission	221
5.10.2	Spin-Polarized Circular Dichroic Resonant Photoemission	221
Chapter 6	X-Ray Absorption Spectroscopy	225
6.1	Basics of X-Ray Absorption Spectroscopy	225
6.1.1	Metal L _{2,3} Edges	228
6.2	Experimental Aspects	228
6.2.1	Transmission Detection	229
6.2.2	Energy Dispersive X-Ray Absorption	229
6.2.3	Fluorescence Yield	229
6.2.4	Self-Absorption Effects in Fluorescence Yield Detection	230
6.2.5	Nonlinear Decay Ratios and Distortions in Fluorescence Yield Spectra	230
6.2.6	Partial Fluorescence Yield	230
6.2.7	Electron Yield	231
6.2.8	Partial Electron Yield	231
6.2.9	Ion Yield	232
6.2.10	Detection of an EELS Spectrum	232
6.2.11	Low-Energy EELS Experiments	233
6.2.12	Space: X-Ray Spectromicroscopy and TEM-EELS	233
6.2.13	Time-Resolved X-Ray Absorption	234
6.2.14	Extreme Conditions	235
6.3	L _{2,3} Edges of 3d TM Systems	235
6.3.1	3d ⁰ Systems	236
6.3.2	3d ¹ Systems	237
6.3.2.1	VO ₂ and LaTiO ₃	237
6.3.3	3d ² Systems	237
6.3.4	3d ³ Systems	238
6.3.5	3d ⁴ Systems	239
6.3.5.1	LaMnO ₃	240
6.3.5.2	Mixed Spin Ground State in LiMnO ₂	240

6.3.6	3d ⁵ Systems	241
6.3.6.1	MnO	241
6.3.6.2	Fe ₂ O ₃	242
6.3.6.3	Fe ³⁺ (tacn) ₂	243
6.3.6.4	Fe ³⁺ (CN) ₆	243
6.3.6.5	Intermediate Spin State of SrCoO ₃	244
6.3.7	3d ⁶ Systems	245
6.3.7.1	Effect of 3d Spin–Orbit Coupling in Fe ₂ SiO ₄	246
6.3.7.2	Co ³⁺ Oxides	247
6.3.8	3d ⁷ Systems	248
6.3.8.1	Effects of 3d Spin–Orbit Coupling on the Ground State of Co ²⁺	248
6.3.8.2	Mixed Spin Ground State in PrNiO ₃	249
6.3.9	3d ⁸ Systems	251
6.3.9.1	NiO	251
6.3.9.2	High-Spin and Low-Spin Ni ²⁺ and Cu ³⁺ Systems	251
6.3.10	3d ⁹ Systems	253
6.4	Other X-Ray Absorption Spectra of the 3d TM Systems	254
6.4.1	TM M _{2,3} Edges	254
6.4.2	TM M _i Edges	255
6.4.3	TM K Edges	255
6.4.4	Ligand K Edges	260
6.4.4.1	Oxygen K Edges of High T _c Copper Oxides	264
6.4.5	Soft X-Ray K Edges by X-Ray Raman Spectroscopy	264
6.4.5.1	Modifying the Selection Rules	265
6.5	X-Ray Absorption Spectra of the 4d and 5d TM Systems	265
6.5.1	L _{2,3} Edges of 4d TM Systems	266
6.5.2	Picosecond Time-Resolved 2p XAS Spectra of [Ru(bpy) ₃] ²⁺	268
6.5.3	Higher Valent Ruthenium Compounds	269
6.5.4	Pd L Edges and the Number of 4d Holes in Pd Metal	270
6.5.5	X-Ray Absorption Spectra of the 5d Transition Metals	271
6.6	X-Ray Absorption Spectra of the 4f RE and 5f Actinide Systems	272
6.6.1	M _{4,5} Edges of Rare Earths	273
6.6.1.1	M _{4,5} Edge of Tm	274
6.6.1.2	M _{4,5} Edge of La ³⁺	277
6.6.1.3	M _{4,5} Edge of CeO ₂	278
6.6.2	N _{4,5} Edges of Rare Earths	278
6.6.3	L _{2,3} Edges of Rare Earths	281
6.6.4	O _{4,5} Edges of Actinides	282
6.6.5	M _{4,5} Edges of Actinides	282
Chapter 7	X-Ray Magnetic Circular Dichroism	287
7.1	Introduction	287
7.2	XMCD Effects in the L _{2,3} Edges of TM Ions and Compounds	288
7.2.1	Atomic Single Electron Model	288
7.2.2	XMCD Effects in Ni ²⁺	293

7.2.3	XMCD of CrO_2	297
7.2.4	Magnetic X-Ray Linear Dichroism	297
7.2.5	Orientation Dependence of XMCD and XMLD Effects	298
7.2.6	XMLD for Doped LaMnO_3 Systems	299
7.3	Sum Rules	299
7.3.1	Sum Rules for Orbital and Spin Moments	299
7.3.2	Application of the Sum Rules to Fe and Co Metals	302
7.3.3	Application of the Sum Rules to Au/Co-Nanocluster/ Au Systems	304
7.3.4	Limitations of the Sum Rules	308
7.3.5	Theoretical Simulations of the Spin Sum Rule	309
7.4	XMCD Effects in the K Edges of Transition Metals	310
7.4.1	X-Ray Natural Circular Dichroism and X-Ray Optical Activity	311
7.5	XMCD Effects in the M Edges of Rare Earths	312
7.5.1	XMCD and XMLD Effects from Atomic Multiplets	312
7.5.2	Temperature Effects on the XMCD and XMLD	314
7.6	XMCD Effects in the L Edges of Rare Earth Systems	314
7.6.1	Effects of 4f5d Exchange Interaction	315
7.6.2	Contribution of Electric Quadrupole Transition	319
7.6.3	Effect of Hybridization between RE 5d and TM 3d States	319
7.6.4	XMCD at L Edges of $\text{R}_2\text{Fe}_{14}\text{B}$ (R = La–Lu)	320
7.6.5	Mixed Valence Compound CeFe_2	324
7.6.6	Multielectron Excitations	328
7.7	Applications of XMCD	329
7.7.1	Magnetic Oxides	329
7.7.2	Thin Magnetic (Multi)layers, Interface, and Surface Effects	330
7.7.3	Impurities, Adsorbates, and Metal Chains	332
7.7.4	Magnetic Nanoparticles and Catalyst Materials	333
7.7.5	Molecular Magnets	333
7.7.6	Metal Centers in Proteins	334
Chapter 8	Resonant X-Ray Emission Spectroscopy	335
8.1	Introduction	335
8.1.1	Experimental Aspects of XES (RXES and NXES)	337
8.1.1.1	Detectors for Soft X-Ray XES	338
8.1.1.2	Detectors for Hard X-Ray XES	338
8.1.1.3	X-Ray Raman Allows Soft X-Ray XAS under Extreme Conditions	338
8.1.2	Basic Description and Some Theoretical Aspects	338
8.2	Rare Earth Compounds	343
8.2.1	Effect of Intra-Atomic Multiplet Coupling	343
8.2.2	Effect of Interatomic Hybridization in CeO_2 and PrO_2	348
8.2.3	Metallic Ce Compounds with Mixed-Valence Character	351
8.2.4	Kondo Resonance in Yb Compounds	354

8.2.5	Dy 2p3d RXES Detection of the 2p4f EQ Excitation	357
8.2.6	EQ Excitations in Light Rare Earth Elements	360
8.3	High T_c Cuprates and Related Materials	363
8.3.1	Cu 2p3d RXES	363
8.3.2	Cu 1s4p RXES	367
8.3.3	Cu 1s2p RXES	373
8.3.4	O 1s2p RXES	377
8.4	Nickel and Cobalt Compounds	380
8.4.1	Ni 2p3d RXES in NiO: Charge Transfer Excitations	380
8.4.2	Ni 2p3d RXES in NiO: dd Excitations	384
8.4.3	Ni 2p3d RXES in NiO: Spin-Flip Excitations	386
8.4.4	Ni 1s4p RXES of NiO: Pressure Dependence	387
8.4.5	Co 2p3d RXES in CoO and Other Co Compounds	389
8.4.6	Co 1s2p RXES of CoO: Effect of Resolution	389
8.4.7	Co 1s2p RXES: Nonlocal Dipole Transitions	391
8.5	Iron and Manganese Compounds	393
8.5.1	Fe 1s2p RXES of Iron Oxides: 2D RXES Images	393
8.5.2	HERFD-XAS of Iron Oxides	395
8.5.3	Fe 2p XAS Spectra Measured at the Fe K Edge	397
8.5.4	Valence Selective XAS	397
8.5.5	Mn 2p3d RXES of MnO	399
8.5.6	Mn 2p3d RXES: Interplay of dd and Charge Transfer Excitations	402
8.5.7	Mn 1s4p RXES of LaMnO_3	405
8.5.8	Mn and Ni 1s3p XES: Chemical Sensitivity	406
8.5.9	Mn 1s3p XES: K Capture Versus X-Ray Ionization	408
8.5.9.1	Atomic Multiplet Calculation	409
8.5.9.2	LFM Calculation	410
8.5.9.3	Charge Transfer Multiplet Calculation	410
8.5.9.4	Coherent Calculation of Mn 1s3p NXES Spectra	411
8.6	Early Transition Metal Compounds	412
8.6.1	Ca 2p3s RXES in CaF_2	413
8.6.2	Ti 2p3d RXES of TiO_2 : Polarization Dependence	415
8.6.3	Sc 2p3d RXES of the ScF_3 , ScCl_3 , and ScBr_3	420
8.6.4	TM 2p3d RXES of d^n ($n = 1, 2, 3$) Systems	420
8.6.5	V 2p3d RXES of Vanadium Oxides	423
8.7	Electron Spin States Detected by RXES and NXES	423
8.7.1	Local Spin-Selective Excitation Spectra	423
8.7.2	Spin-Dependent TM 1s3p NXES Spectra	425
8.7.3	TM 1s3p NXES and Spin-Transitions	426
8.7.4	Local-Spin Selective XAS and XMCD	429
8.8	MCD in RXES of Ferromagnetic Systems	429
8.8.1	Longitudinal and Transverse Geometries in MCD-RXES	429
8.8.2	MCD-RXES in LG of CeFe_2	433
8.8.3	Experiments and Theory of MCD-RXES in TG	435