Core Level Spectroscopy of Solids

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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

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Akio Kotani

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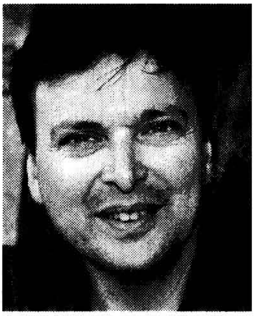
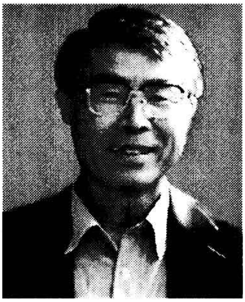
Authors



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.

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