

# Photoemission in Solids I

General Principles

Edited by M. Cardona and L. Ley

With Contributions by

M. Cardona P. H. Citrin L. Ley S. T. Manson  
W. L. Schaich D. A. Shirley N. V. Smith  
G. K. Wertheim

With 90 Figures

Springer-Verlag Berlin Heidelberg New York 1978

Professor Dr. *Manuel Cardona*  
Dr. *Lothar Ley*

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1  
D-7000 Stuttgart 80, Fed. Rep. of Germany

ISBN 3-540-08685-4 Springer-Verlag Berlin Heidelberg New York  
ISBN 0-387-08685-4 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Photoemission in solids. (Topics in applied physics; v. 26). Includes bibliographies and index. General principles. — 1. Photoelectron spectroscopy. 2. Solids—Spectra. 3. Photoemission. I. Cardona, Manuel, 1934—. II. Ley, Lothar, 1943—. QC454.P48P49 530.4'1 78-2503

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law, where copies are made for other than private use, a fee is payable to the publisher, the amount of the fee to be determined by agreement with the publisher.

© by Springer-Verlag Berlin Heidelberg 1978  
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Monophoto typesetting, offset printing and bookbinding: Brühlsche Universitätsdruckerei, Lahn-Gießen  
2153/3130-543210

## Preface

This book is devoted to the phenomenon of photoemission in solids or, more specifically, to photoelectron spectroscopy as applied to the investigation of the electronic structure of solids. The phenomenon is simple: a sample is placed in vacuum and irradiated with monochromatic (or as monochromatic as possible) photons of sufficient energy to excite electrons into unbound states. Electrons are then emitted into vacuum carrying information about the states they came from (or, more accurately, about the state *left behind*). This information can be extracted by investigating the properties of the outgoing electrons (velocity distribution, angle of emission, polarization). Photoelectron spectroscopy yields information sometimes similar and sometimes complementary to that obtained with other spectroscopic techniques such as photon absorption and scattering, characteristic electron energy losses, and x-ray fluorescence.

The potential of photoelectron spectroscopy for investigating electronic levels was recognized by H. Robinson and by M. de Broglie shortly after the discovery of the phenomenon of photoemission by H. Hertz and its interpretation by A. Einstein. However, due to the inadequacies of the available equipment, this method was soon overshadowed by developments in the field of x-ray absorption and emission spectroscopy. Commercial interest in the development of photocathodes and theoretical progress in the understanding of electronic states in solids produced new fundamental interest in photoelectron spectroscopy during the late 1950's. This interest was paralleled by an unprecedented development in experimental techniques, including ultrahigh vacuum technology, photon sources, spectrometers, and detectors. This development has continued to the present day as the number of commercially available spectrometers multiplies, spurred, in part, by practical applications of the method such as chemical analysis and the investigation of catalytic processes.

Photoelectron spectroscopy can be and has been used to study almost any kind of solids: metals, semiconductors, insulators, magnetic materials, glasses, etc. The purpose of the present book is to give the foundations and specific examples of these applications while covering as wide a range of topics of current interest as possible. We have, however, deliberately omitted a complete discussion of surface effects (except for semiconductors) and adsorbed surface layers because of the recent availability of other monographs. Two different methods of photoelectron spectroscopy have coexisted since their inception. One of them uses as photon sources gas discharge lamps (usually uv, hence ultraviolet photoelectron spectroscopy or UPS), the other, x-ray tubes (XPS).

In the past few years many experimental systems have been built with both x-rays and uv capabilities. Also, the dividing line between UPS and XPS has disappeared as synchrotron radiation has become more popular as a photon source.

This Topics volume is designed along the following guidelines. The tutorial Chapter 1 discusses the general principles and capabilities of the method in the perspective of other related spectroscopic techniques such as x-ray fluorescence, Auger spectroscopy, characteristic energy losses, etc. The current experimental techniques are reviewed. An extensive discussion of the theory and experimental determinations of the work function is given, a subject which is not treated in the rest of the work. Chapter 2 presents the formal, first principles theory of photoemission and follows the assumptions required to break it up into the current phenomenological models, such as the three-step model. One of these steps is the photoexcitation of a valence or core electron. The simplest model of this process, and one which usually applies to core electrons, is the photoionization of atoms. Chapter 3 treats the theory of partial photoionization cross sections of atoms. Chapter 4 discusses a number of phenomena which go beyond the one-electron picture of atoms and solids, such as relaxation, configuration interaction, and inelastic processes. One of these processes, the simultaneous excitation of a large number of electrons near the Fermi energy which accompanies photoemission from core levels in a metal, is treated in detail in Chapter 5. Finally, Chapter 6 contains a discussion of the increasingly popular method of angular resolved photoemission. A table of binding energies of core electrons in atoms completes the volume.

There will be a companion volume (Topics in Applied Physics, Vol. 27) which is devoted to case studies dealing with semiconductors, transition metals, rare earths, organic compounds, synchrotron radiation, and simple metals. The complete Contents of Volume 27 is included at the end of this book.

The editors have profited enormously from the experience and help of their colleagues at the Max-Planck-Institut für Festkörperforschung, the University of California, Berkeley, and the Deutsches Elektronen-Synchrotron DESY. There is no need to mention their names explicitly since they appear profusely throughout the references to the various chapters. Thanks are also due to all of the contributors for keeping the deadlines and for their willingness and patience in following the editors' suggestions.

Stuttgart, May 1978

*Manuel Cardona  
Lothar Ley*

# Contents

<b>1. Introduction.</b> By M.Cardona and L.Ley (With 26 Figures)	1
1.1 Historical Remarks	3
1.1.1 The Photoelectric Effect in the Visible and Near uv: The Early Days	3
1.1.2 Photoemissive Materials: Photocathodes	6
1.1.3 Photoemission and the Electronic Structure of Solids	8
1.1.4 X-Ray Photoelectron Spectroscopy (ESCA, XPS)	10
1.2 The Work Function	16
1.2.1 Methods to Determine the Work Function	17
1.2.2 Thermionic Emission	19
1.2.3 Contact Potential: The Kelvin Method	22
The Break Point of the Retarding Potential Curve	22
The Electron Beam Method	22
1.2.4 Photoyield Near Threshold	23
1.2.5 Quantum Yield as a Function of Temperature	27
1.2.6 Total Photoelectric Yield	28
1.2.7 Threshold of Energy Distribution Curves (EDC)	28
1.2.8 Field Emission	29
1.2.9 Calorimetric Method	31
1.2.10 Effusion Method	31
1.3 Theory of the Work Function	32
1.3.1 Simple Metals	34
1.3.2 Simple Metals: Surface Dipole Contribution	38
1.3.3 Volume and Temperature Dependence of the Work Function	41
1.3.4 Effect of Adsorbed Alkali Metal Layers	43
1.3.5 Transition Metals	44
1.3.6 Semiconductors	46
1.3.7 Numerological and Phenomenological Theories	48
1.4 Techniques of Photoemission	52
1.4.1 The Photon Source	52
1.4.2 Energy Analyzers	55
1.4.3 Sample Preparation	57
Cleaning Procedures	58
1.5 Core Levels	60
1.5.1 Elemental Analysis	60

1.5.2 Chemical Shifts . . . . .	60
Theoretical Models for the Calculation of Binding Energy Shifts . . . . .	63
Core Level Shifts of Rare Gas Atoms Implanted in Noble Metals . . . . .	70
Binding Energies in Ionic Solids . . . . .	73
Chemical Shifts in Alloys . . . . .	74
1.5.3 The Width of Core Levels . . . . .	76
1.5.4 The Core Level Cross Sections . . . . .	80
1.6 The Interpretation of Valence Band Spectra . . . . .	84
1.6.1 The Three-Step Model of Photoemission . . . . .	84
1.6.2 Beyond the Isotropic Three-Step Model . . . . .	89
References . . . . .	93

## 2. Theory of Photoemission: Independent Particle Model

By W.L.Schaich (With 2 Figures) . . . . .	105
2.1 Formal Approaches . . . . .	106
2.1.1 Quadratic Response . . . . .	106
2.1.2 Many-Body Features . . . . .	109
2.2 Independent Particle Reduction . . . . .	109
2.2.1 Golden Rule Form . . . . .	109
2.2.2 Comparison With Scattering Theory . . . . .	113
2.2.3 Theoretical Ingredients . . . . .	117
2.3 Model Calculations . . . . .	119
2.3.1 Simplification of Transverse Periodicity . . . . .	119
2.3.2 Volume Effect Limit . . . . .	122
2.3.3 Surface Effects . . . . .	128
2.4 Summary . . . . .	131
References . . . . .	132

## 3. The Calculation of Photoionization Cross Sections: An Atomic View

By S.T.Manson (With 16 Figures) . . . . .	135
3.1 Theory of Atomic Photoabsorption . . . . .	136
3.1.1 General Theory . . . . .	136
3.1.2 Reduction of the Matrix Element to the Dipole Approximation . . . . .	137
3.1.3 Alternate Forms of the Dipole Matrix Element . . . . .	138
3.1.4 Relationship to Density of States . . . . .	140
3.2 Central Field Calculations . . . . .	140
3.3 Accurate Calculations of Photoionization Cross Sections . . . . .	149
3.3.1 Hartree-Fock Calculations . . . . .	150

3.3.2 Beyond the Hartree-Fock Calculation: The Effects of Correlation . . . . .	156
3.4 Concluding Remarks . . . . .	159
References . . . . .	160

#### **4. Many-Electron and Final-State Effects: Beyond the One-Electron**

<b>Picture.</b> By D. A. Shirley (With 10 Figures) . . . . .	165
4.1 Multiplet Splitting . . . . .	165
4.1.1 Theory . . . . .	165
4.1.2 Transition Metals . . . . .	167
4.1.3 Rare Earths . . . . .	170
4.2 Relaxation . . . . .	174
4.2.1 The Energy Sum Rule . . . . .	175
4.2.2 Relaxation Energies . . . . .	176
Atomic Relaxation . . . . .	176
Extra-Atomic Relaxation . . . . .	177
4.3 Electron Correlation Effects . . . . .	181
4.3.1 The Configuration Interaction Formalism . . . . .	182
Final-State Configuration Interaction (FSCI) . . . . .	182
Continuum-State Configuration Interaction (CSCI) . . . . .	184
Initial-State Configuration Interaction (ISCI) . . . . .	184
4.3.2 Case Studies . . . . .	186
Final-State Configuration Interactions:	
The 4 <i>p</i> Shell of Xe-Like Ions . . . . .	186
Continuum-State Configuration Interaction: The 5 <i>p</i> <sup>6</sup> 6 <i>s</i> <sup>2</sup> Shell . . . . .	187
Initial-State Configuration: Two Closed-Shell Cases . . . . .	189
4.4 Inelastic Process . . . . .	189
4.4.1 Intrinsic and Extrinsic Structure . . . . .	190
4.4.2 Surface Sensitivity . . . . .	192
References . . . . .	193

#### **5. Fermi Surface Excitations in X-Ray Photoemission Line Shapes from**

<b>Metals.</b> By G. K. Wertheim and P. H. Citrin (With 22 Figures) . . . . .	197
5.1 Overview . . . . .	197
5.2 Historical Background . . . . .	198
5.2.1 The X-Ray Edge Problem . . . . .	198
5.2.2 X-Ray Emission and Photoemission Spectra . . . . .	200
5.3 The X-Ray Photoemission Line Shape . . . . .	201
5.3.1 Behavior Near the Singularity . . . . .	201
5.3.2 Extrinsic Effects in XPS . . . . .	206
5.3.3 Data Analysis . . . . .	208

5.4 Discussion of Experimental Results . . . . .	210
5.4.1 The Simple Metals Li, Na, Mg, and Al . . . . .	210
5.4.2 The Noble Metals . . . . .	225
5.4.3 The <i>s-p</i> Metals Cd, In, Sn, and Pb . . . . .	227
5.4.4 The Transition Metals and Alloys . . . . .	229
5.5 Summary . . . . .	234
References . . . . .	234
 <b>6. Angular Dependent Photoemission. By N. V. Smith</b>	
(With 14 Figures) . . . . .	237
6.1 Preliminary Discussion . . . . .	237
6.1.1 Energetics . . . . .	238
6.1.2 Theoretical Perspective . . . . .	240
6.2 Experimental Systems . . . . .	241
6.2.1 General Considerations . . . . .	241
6.2.2 Movable Analyzer . . . . .	242
6.2.3 Modified Analyzer . . . . .	243
6.2.4 Multidetector Systems . . . . .	244
6.3 Theoretical Approaches . . . . .	246
6.3.1 Pseudopotential Model . . . . .	246
6.3.2 Orbital Information . . . . .	249
6.3.3 One-Step Theories . . . . .	252
6.4 Selected Results . . . . .	254
6.4.1 Layer Compounds . . . . .	254
6.4.2 Three-Dimensional Band Structures . . . . .	257
6.4.3 Normal Emission . . . . .	259
6.4.4 Nonnormal CFS . . . . .	261
References . . . . .	263
 <b>Appendix: Table of Core-Level Binding Energies . . . . .</b>	<b>265</b>
 <b>Contents of Photoemission in Solids II . . . . .</b>	<b>277</b>
 <b>Additional References with Titles . . . . .</b>	<b>283</b>
 <b>Subject Index . . . . .</b>	<b>285</b>



## Contributors

Cardona, Manuel

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1  
D-7000 Stuttgart 80, Fed. Rep. of Germany

Citrin, Paul H.

Bell Laboratories, Murray Hill, NJ 07974, USA

Ley, Lothar

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1  
D-7000 Stuttgart 80, Fed. Rep. of Germany

Manson, Steven T.

Department of Physics, Georgia State University,  
Atlanta, GA 30303, USA

Schaich, William L.

Physics Department, Indiana University,  
Bloomington, IN 47401, USA

Shirley, David A.

Materials and Molecular Research Division,  
Lawrence Berkeley Laboratory, and Department of Chemistry,  
University of California, Berkeley, CA 94720, USA

Smith, Neville V.

Bell Laboratories, Murray Hill, NJ 07974, USA

Wertheim, Gunther K.

Bell Laboratories, Murray Hill, NJ 07974, USA