

# Contents

<b>1. Introduction.</b> By L. Ley and M. Cardona . . . . .	1
1.1 Survey of Previous Volume . . . . .	4
1.2 Contents of Present Volume . . . . .	8
References . . . . .	9
<b>2. Photoemission in Semiconductors</b>	
By L. Ley, M. Cardona, and R. A. Pollak (With 97 Figures) . . . . .	11
2.1 Background . . . . .	11
2.1.1 Historical Survey . . . . .	13
2.2 Band Structure of Semiconductors . . . . .	15
2.2.1 Tetrahedral Semiconductors . . . . .	15
2.2.2 Semiconductors with an Average of Five Valence Electrons per Atom . . . . .	28
2.2.3 Selenium, Tellurium, and the $V_2VI_3$ Compounds . . . . .	30
2.2.4 Transition Metal Dichalcogenides . . . . .	32
2.3 Methods Complementary to Photoelectron Spectroscopy . . . . .	40
2.3.1 Optical Absorption, Reflection, and Modulation Spectros- copy . . . . .	40
2.3.2 Characteristic Electron Energy Losses . . . . .	43
2.3.3 X-Ray Emission Spectroscopy . . . . .	45
2.4 Volume Photoemission: Angular Integrated EDC's from Valence Bands . . . . .	47
2.4.1 Band-Structure Regime: Germanium . . . . .	51
2.4.2 XPS Regime: Tetrahedral Semiconductors . . . . .	55
2.4.3 XPS Regime: IV-VI Compounds . . . . .	62
2.4.4 Partial Density of Valence States: Copper and Silver Halides; Chalcopyrites; Transition Metal, Rare Earth, and Actinide Compounds . . . . .	67
2.4.5 Layer Structures: Transition Metal Dichalcogenides . . . . .	72
2.4.6 Layer Structures: $SnS_2$ , $SnSe_2$ , $PbI_2$ , GaS, GaSe . . . . .	75
2.5 Photoemission and Density of Conduction States . . . . .	78
2.5.1 Secondary Electron Tails . . . . .	79
2.5.2 Partial Yield Spectroscopy . . . . .	79
2.6 Angular Resolved Photoemission from the Lead Salts . . . . .	80

2.7	Amorphous Semiconductors . . . . .	85
2.7.1	Tetrahedrally Coordinated Amorphous Semiconductors . . . . .	87
	a) Amorphous Si and Ge . . . . .	87
	b) Amorphous III–V Compounds . . . . .	100
2.7.2	Amorphous Semiconductors with an Average of Five Valence Electrons per Atom . . . . .	104
2.7.3	Amorphous Group VI Semiconductors . . . . .	111
2.7.4	Gap States in Amorphous Semiconductors . . . . .	114
2.8	Ionicity . . . . .	118
2.8.1	An Ionicity Scale Based on Valence Band Spectra . . . . .	121
2.8.2	Binding Energy Shift and Charge Transfer . . . . .	126
2.9	Photoemission Spectroscopy of Semiconductor Surfaces . . . . .	130
2.9.1	Semiconductor Surface States . . . . .	131
2.9.2	Silicon Surface States . . . . .	133
	a) Photoemission from Si(111) $2 \times 1$ and $7 \times 7$ Surfaces . . . . .	135
	b) Electronic Structure Theory of Si(111) Surfaces . . . . .	141
2.9.3	Surface States of Group III–V Semiconductors . . . . .	148
2.9.4	Surface Chemistry of Semiconductors — Si(111): H and Si(111): SiH <sub>3</sub> . . . . .	151
2.9.5	Interface States: Metal-Semiconductor Electrical Barriers . . . . .	154
	References . . . . .	158

### 3. Unfilled Inner Shells: Transition Metals and Compounds

	By S. Hüfner (With 25 Figures) . . . . .	173
3.1	Overview . . . . .	173
3.2	Transition Metal Compounds . . . . .	176
3.2.1	The Hubbard Model . . . . .	176
3.2.2	Final State Effects in Photoemission Spectra . . . . .	177
	a) Satellites . . . . .	177
	b) Multiplet and Crystal-Field Splitting . . . . .	179
3.2.3	Transition Metal Oxides . . . . .	183
	a) MnO, CoO, NiO: Mott Insulators . . . . .	183
	b) VO <sub>2</sub> : A Nonmetal-Metal Transition . . . . .	188
	c) ReO <sub>3</sub> : A Typical Metal . . . . .	189
3.2.4	Miscellaneous Compounds . . . . .	191
3.2.5	The Correlation Energy U . . . . .	191
3.3	<i>d</i> -Band Metals: Introduction . . . . .	192
3.3.1	The Noble Metals: Cu, Ag, Au . . . . .	194
3.3.2	The Ferromagnets: Fe, Co, Ni . . . . .	200
3.3.3	Nonmagnetic <i>d</i> -Band Metals . . . . .	205
3.4	Alloys . . . . .	206
3.4.1	Dilute Alloys: The Friedel-Anderson Model . . . . .	206
3.4.2	Concentrated Alloys: The Coherent Potential Approximation . . . . .	210
3.5	Intermetallic Compounds . . . . .	212
3.6	Summary, Outlook . . . . .	212
	References . . . . .	213

#### 4. Unfilled Inner Shells: Rare Earths and Their Compounds

By M. Campagna, G. K. Wertheim, and Y. Baer (With 35 Figures)	217
4.1 Background	217
4.1.1 Where Are the $4f$ Levels Located?	217
4.1.2 Multiplet Intensities Versus Total Photoelectric Cross Sections at 1.5 keV	218
4.1.3 Renormalized Atom Scheme and Thermodynamics	221
4.1.4 Multiplet and Satellite Structure in Photoemission from Core Levels Other than $4f$	226
4.2 Techniques	227
4.2.1 The Need of High Resolution in Rare-Earth Studies	227
4.2.2 Sample Preparation	228
a) Pure Metals	228
b) Chalcogenides, Borides, and Alloys	229
4.3 Results	229
4.3.1 Metals	229
a) Identification of the Outermost Levels	229
b) The Light Rare Earths	230
c) The Heavy Rare Earths	233
d) Cerium	235
e) The $4f$ Promotion Energy	237
4.3.2 Compounds and Alloys: Stable $4f^n$ Configurations	237
a) Rare-Earth Halides	237
b) Chalcogenides and Pnictides	238
c) Phonon Broadening in EuO	243
d) Interatomic Auger Transitions in Rare-Earth Borides	245
e) Rare-Earth Intermetallics	249
f) $4s$ and $5s$ Multiplet Splittings	250
g) Spectra of $3d$ and $4d$ Electrons of Rare-Earth Solids	251
h) $4f$ and $4d$ Binding Energy: Atom Versus Solid	253
4.3.3 Intermediate Valence (IV) Compounds	254
a) The Intra-Atomic Coulomb Correlation Energy $U_{\text{eff}}$	257
4.4 Conclusions and Outlook	257
References	258

#### 5. Photoemission from Organic Molecular Crystals

By W. D. Grobman and E. E. Koch (With 14 Figures)	261
5.1 Some Experimental Aspects of Photoemission from Organic Molecular Crystals	262
5.1.1 Charging Effects	262
5.1.2 Secondary Electron Background	264
5.1.3 Electron Attenuation Length (Escape Depth) $\lambda_e(E)$	264
5.1.4 Vacuum Requirements	265
5.1.5 Effects of the Transmission Function of the Electron Energy Analyzer	265
5.2 Band Formation in Linear Alkanes	266

5.3	Aromatic Hydrocarbons . . . . .	267
5.3.1	Acene . . . . .	268
5.3.2	Organometallic Phenyl Compounds . . . . .	270
5.3.3	Anthracene . . . . .	272
5.4	Photoemission Induced by Exciton Annihilation . . . . .	275
5.5	Photoemission from Biological Materials . . . . .	278
5.5.1	Phthalocyanines . . . . .	278
5.5.2	Nucleic Acid Bases . . . . .	280
5.6	Valence Orbital Spectroscopy of Molecular Organic Conductors . . . . .	280
5.6.1	Valence Bands of TTF-TCNQ and Related Compounds . . . . .	280
5.6.2	Valence Bands of (SN) <sub>x</sub> . . . . .	285
5.6.3	The Absence of a Fermi Edge in Photoemission Spectra of Organic "Metals" . . . . .	287
5.7	Core Orbital Spectroscopy of Organic Molecular Crystals . . . . .	288
5.7.1	Solid-State Effects on Core Levels in Charge Transfer Salts . . . . .	288
5.7.2	Core Level Spectroscopy and Charge Transfer in TTF-TCNQ . . . . .	292
5.7.3	Conclusions . . . . .	293
	References . . . . .	294
<b>6.</b>	<b>Synchrotron Radiation: Overview. By C. Kunz (With 33 Figures)</b> . . . . .	<b>299</b>
6.1	Overview . . . . .	300
6.2	Properties of Synchrotron Radiation . . . . .	301
6.2.1	Basic Equations . . . . .	301
6.2.2	Comparison with Other Sources . . . . .	305
6.2.3	Evolution of Synchrotron Sources . . . . .	306
6.3	Arrangement of Experiments . . . . .	310
6.3.1	Layout of Laboratories . . . . .	310
6.3.2	Monochromators . . . . .	311
6.4	Spectroscopic Techniques . . . . .	313
6.4.1	Spectroscopy of Directly Excited Electrons . . . . .	313
6.4.2	Energy Distribution Curves (EDC) . . . . .	314
6.4.3	Constant Final-State Spectroscopy (CFS) . . . . .	316
6.4.4	Constant Initial-State Spectroscopy (CIS) . . . . .	317
6.4.5	Angular Resolved Photoemission (ARP, ARPES) . . . . .	319
6.4.6	Secondary Processes . . . . .	319
6.4.7	Photoelectron Yield Spectroscopy (PEYS) . . . . .	322
6.4.8	Yield Spectroscopy at Oblique Incidence . . . . .	323
6.5	Applications of Yield Spectroscopy . . . . .	326
6.5.1	Anisotropy in the Absorption Coefficient of Se . . . . .	326
6.5.2	Investigation of Alloys . . . . .	328
6.5.3	Investigation of Liquid Metals . . . . .	329
6.6	Experiments Investigating Occupied and Empty States . . . . .	330
6.6.1	Valence Bands in Rare-Gas Solids . . . . .	330
6.6.2	Conduction Band State from Angular Dependent Photoemission . . . . .	333

6.7 Experiments on Relaxation Processes and Excitons . . . . .	335
6.7.1 Phonon Broadening of Core Lines . . . . .	335
6.7.2 Exciton Effects with Core Excitations . . . . .	337
6.7.3 Energy Transfer Processes . . . . .	339
6.8 Surface States and Adsorbates . . . . .	341
6.8.1 Surface Core Excitons on NaCl . . . . .	341
6.8.2 Adsorbates and Oxidation . . . . .	343
References . . . . .	344
<b>7. Simple Metals</b>	
By P.Steiner, H.Höchst, and S.Hüfner (With 10 Figures) . . . . .	349
7.1 Historical Background . . . . .	349
7.2 Theory of the Photoelectron Spectrum . . . . .	351
7.3 Core Level Spectra . . . . .	357
7.4 Valence Band Spectra . . . . .	364
7.5 Summary . . . . .	369
References . . . . .	370
<b>Appendix: Table of Core-Level Binding Energies</b> . . . . .	373
<b>Additional References with Titles</b> . . . . .	385
<b>Subject Index</b> . . . . .	389