

Contents

1. Introduction. By L. Ley and M. Cardona	1
1.1 Survey of Previous Volume	4
1.2 Contents of Present Volume	8
References	9
 2. Photoemission in Semiconductors	
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) 2×1 and 7×7 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 ₃	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 ₂ : A Nonmetal-Metal Transition	188
c) ReO ₃ : 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 4 <i>f</i> 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 4 <i>f</i>	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 4 <i>f</i> Promotion Energy	237
4.3.2 Compounds and Alloys: Stable 4 <i>fⁿ</i> 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) 4 <i>s</i> and 5 <i>s</i> Multiplet Splittings	250
g) Spectra of 3 <i>d</i> and 4 <i>d</i> Electrons of Rare-Earth Solids	251
h) 4 <i>f</i> and 4 <i>d</i> Binding Energy: Atom Versus Solid	253
4.3.3 Intermediate Valence (IV) Compounds	254
a) The Intra-Atomic Coulomb Correlation Energy U_{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 $(\text{SN})_x$	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
6. Synchrotron Radiation: Overview. By C. Kunz (With 33 Figures)	299
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
 7. Simple Metals	
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
 Appendix: Table of Core-Level Binding Energies	 373
Additional References with Titles	385
Subject Index	389