

# Contents

<b>1. Introduction</b>	<b>1</b>
1.1 The Ground State of Many-Body Systems and the Modes of Excitation	1
1.2 Electronic Excitation in Insulators and the Wannier-Mott Exciton	3
1.3 The Frenkel Exciton	5
1.4 The General Case	6
1.4.1 Effective Mass Approximation	8
1.4.2 The Role of Spin	8
1.4.3 Interplay of Spin-Orbit and Exchange Interactions	9
1.4.4 Davydov Splitting	10
1.4.5 Charge Transfer Excitons	10
1.5 Optical Absorption Spectra	11
1.5.1 Allowed Edge Case	12
1.5.2 Forbidden Edge Case	13
1.5.3 Transition from Frenkel to Wannier-Mott Exciton	13
1.6 The Polariton and Spatial Dispersion	15
1.7 Scope of the Present Book	18
<b>2. Theoretical Aspects of Excitonic Molecules</b>	<b>20</b>
2.1 Fission and Fusion of Excitons vs. Chemical Reaction into Excitonic Molecules	20
2.2 The Excitonic Molecule and Electron-Hole Liquid	23
2.2.1 Binding Energy and Electronic Structure of Excitonic Molecule in a Simple System – CuX	23
2.2.2 The Metallic Droplet and Excitonic Molecule in Many-Valley Structures – Ge and Si	32
2.2.3 The Excitonic Molecule in Many-Valley Systems – TiX and AgX	39
2.2.4 Influence of the Polarizable Lattice and the Effect of Anisotropic Effective Mass – CdS and CdSe	44
2.2.5 The Direct Forbidden Exciton – Cu <sub>2</sub> O	46
2.3 Optical Response of an Excitonic Molecule	47
2.3.1 Luminescence Spectrum	48
2.3.2 Relaxation by Emission of Acoustic Phonons	55
2.3.3 Optical Conversion of Excitons into Excitonic Molecules	60
2.3.4 Giant Two-Photon Absorption	61

2.4	Coherent Optical Phenomena Due to the Excitonic Molecule . . .	69
2.4.1	Hyper-Raman Scattering and Luminescence . . . . .	69
2.4.2	Two-Polariton Scattering Due to the Excitonic Molecule . .	75
2.4.3	Dispersion of the Exciton Polariton and Excitonic Molecule . . . . .	79
2.4.4	Four-Wave Mixing Due to the Excitonic Molecule . . . .	83
2.4.5	Phase-Conjugation by Four-Wave Mixing . . . . .	87
2.5	The Excitonic Molecule at High Densities . . . . .	91
2.5.1	Renormalization of the Exciton Polariton Due to the Excitonic Molecule Giant Two-Photon Absorption . . . .	91
2.5.2	Polarization Rotation Effects Due to Two-Photon Excitation of the Excitonic Molecule . . . . .	95
2.5.3	Multi-Polariton Scattering Via Excitonic Molecules . . . .	102
2.5.4	Optical Bistability Due to the Excitonic Molecule . . . .	106
2.5.5	Relaxation and Bose Condensation of Excitonic Molecules . . . . .	110
<b>3.</b>	<b>The Exciton and Excitonic Molecule in Cuprous Halides . . . . .</b>	<b>116</b>
3.1	Band Structure and Excitonic States . . . . .	116
3.2	Exciton Absorption, Reflection, and Emission Spectra . . . .	117
3.2.1	Absorption and Reflection Spectra . . . . .	117
3.2.2	Splitting of Exciton Bands by Perturbations . . . . .	119
3.2.3	Emission Spectra . . . . .	121
3.2.4	Phonon Structure in the Excitation Spectra of Free-Exciton Emission . . . . .	125
3.2.5	Bound Excitons . . . . .	127
3.2.6	CuCl-CuBr Solid Solutions . . . . .	129
3.3	High-Density Excitation Effects . . . . .	132
3.3.1	Exciton-Electron Interaction . . . . .	132
3.3.2	Effect on Exciton Absorption Bands . . . . .	136
3.3.3	Creation of the Excitonic Molecule by Exciton-Exciton Collision . . . . .	140
3.4	Giant Two-Photon Excitation of the Excitonic Molecule . . . .	144
3.4.1	Evidence of Giant Two-Photon Creation . . . . .	144
3.4.2	Giant Two-Photon Absorption . . . . .	146
3.5	Two-Photon Resonant Raman Scattering Via the Excitonic Molecule . . . . .	148
3.5.1	Backward Scattering . . . . .	148
3.5.2	Forward Scattering . . . . .	150
3.5.3	Scattering with Recoil of the Upper-Branch Polariton . . .	152
3.5.4	Polarization Character – Geometrical Selection Rules . . .	154
3.5.5	Nonlinear Change of Exciton-Polariton Dispersion Associated with the GTA . . . . .	155
3.6	Acoustic-Phonon Interaction of the Excitonic Molecule . . . .	161

3.7	Coexistence of Luminescence and Raman Components in the Resonant Excitation . . . . .	166
3.8	Redistribution of Excitonic Molecules Resonantly Generated by Two-Photon Excitation . . . . .	170
3.8.1	Calculation of Line-Shapes of the Excitonic Molecule Luminescence . . . . .	172
3.9	Relaxation of the Excitonic Molecule Due to Intermolecular Collisions: Influence on the GTA and Secondary Emissions . . . .	174
3.9.1	Effect on the GTA Spectra . . . . .	175
3.9.2	Effect on Secondary Emissions . . . . .	176
3.10	Spatial Dispersion of the Exciton and Excitonic Molecule . . . .	181
3.10.1	CuCl . . . . .	182
3.10.2	CuBr . . . . .	188
3.11	Higher Excited States of the Excitonic Molecule . . . . .	200
<b>4.</b>	<b>Theory of Excitons in Phonon Fields . . . . .</b>	<b>203</b>
4.1	Electron-Phonon Interactions . . . . .	204
4.1.1	Types and Ranges of Electron-Phonon Interactions . . . .	204
4.1.2	The Polaron . . . . .	208
4.1.3	Exciton-Phonon Interactions and the Form Factor . . . .	210
4.1.4	Polaron Effects of an Exciton . . . . .	211
4.2	The Exciton in Spatially Fluctuating Fields . . . . .	212
4.2.1	Localization Versus Delocalization . . . . .	212
4.2.2	Overall Line-Shape of the Absorption Spectra . . . . .	215
4.2.3	Coherent Potential Approximation for an Exciton in a Mixed Crystal and in a Phonon Field . . . . .	220
4.2.4	The Urbach Rule and Exciton Localization . . . . .	228
4.3	Phonon Structures in Exciton Spectra . . . . .	234
4.3.1	Motional Reduction of Phonon Sidebands . . . . .	235
4.3.2	Multicomponent Line-Shape Formula . . . . .	238
4.3.3	The Electron-Hole Relative Motion and the Phonon Sideband of an Exciton . . . . .	242
4.4	Self-Trapping . . . . .	245
4.4.1	Local Stabilities of Free and Self-Trapped States . . . .	245
4.4.2	Continuum Model for Self-Trapping . . . . .	247
4.4.3	Adiabatic Potentials for Self-Trapping . . . . .	250
4.4.4	Effective Mass Change in the F-S Transition . . . . .	254
4.4.5	Extrinsic Self-Trapping and Shallow-Deep Instability . . .	258
4.4.6	Instabilities in the Relative Motion of a Pair of Charged Particles . . . . .	260
4.4.7	Survey of Experimental Studies of Self-Trapping and Related Instabilities . . . . .	264
4.5	Electron-Hole Recombination . . . . .	270
4.5.1	Polariton Bottleneck . . . . .	270

4.5.2	Resonant Secondary Radiation . . . . .	272
4.5.3	Capture, Recombination, and Enhanced Defect Reaction Via a Deep Impurity Level in a Semiconductor . . . . .	273
4.5.4	Self-Trapping and Recombination of an Exciton as a Multiphonon Process . . . . .	275
4.6	Excitonic Instability and Phase Changes . . . . .	276
4.6.1	<i>t-U-S</i> Problem . . . . .	278
4.6.2	Two-Site Two-Electron System . . . . .	278
4.6.3	Hückel's ( $4n + 2$ ) Rule for Ring Systems . . . . .	280
4.6.4	One-Dimensional Hubbard-Peierls System . . . . .	282
4.6.5	Prospects . . . . .	283
<b>5.</b>	<b>Excitons in Condensed Rare Gases . . . . .</b>	<b>285</b>
5.1	Electronic Structure of Condensed Rare Gases . . . . .	286
5.2	Charge Carriers in Condensed Rare Gases . . . . .	288
5.3	Excitons and Exciton-Phonon Interactions in Condensed Rare Gases . . . . .	290
5.3.1	Exciton Absorption Spectra . . . . .	292
5.3.2	Nature of Relaxed Excitons in Condensed Rare Gases . . . . .	295
5.3.3	Formation of Self-Trapped Exciton Bubbles in Condensed Neon . . . . .	300
5.3.4	Relaxation of Free Excitons in Photo-Excited Rare Gas Solids . . . . .	305
<b>6.</b>	<b>Exciton-Phonon Processes in Silver Halides . . . . .</b>	<b>309</b>
6.1	Electronic and Lattice Properties of Silver Halides . . . . .	309
6.2	Excitons and Exciton-Phonon Interactions in Silver Halides . . . . .	316
6.2.1	Exciton Transitions in Pure Crystals . . . . .	317
6.2.2	Exciton Transitions in Mixed Crystals . . . . .	331
6.2.3	Bound-Exciton Transitions at an Isoelectronic Iodine Impurity . . . . .	339
6.3	Relaxation Processes of Photo-Excited States in Silver and Alkali Halides . . . . .	347
6.4	Localized Electrons and Holes in Silver Halides . . . . .	351
6.4.1	Nature of Localized Centers in Silver Halides Compared to Color Centers in Alkali Halides . . . . .	352
6.4.2	Bound Polarons in Silver and Alkali Halides . . . . .	358
6.4.3	Photochemical Reactions in Silver Halides at Higher Temperatures . . . . .	364
<b>7.</b>	<b>Excitons and Their Interactions with Phonons and External Fields in Thallous Halides . . . . .</b>	<b>370</b>
7.1	Band Structures and Exciton States of Thallous Halides . . . . .	371
7.1.1	Thallous Halides . . . . .	371

7.1.2	Band Structures . . . . .	372
7.1.3	Exciton States . . . . .	374
7.2	Optical Spectra of Thallous Halides . . . . .	378
7.2.1	Absorption and Reflection Spectra in a Wide Energy Range . . . . .	378
7.2.2	Spectra of $X_6^+ \times X_6^-$ Direct Excitons . . . . .	380
7.2.3	Spectra of $X_6^+ \times R_6^-$ Indirect Excitons . . . . .	388
7.2.4	Free-Exciton Emission . . . . .	392
7.2.5	Excitonic Molecules of $X_6^+ \times R_6^-$ Excitons . . . . .	398
7.3	Resonant Raman Scattering by Excitons in Thallous Halides . . . . .	403
7.3.1	LO Phonon Scattering Resonant to a Direct Exciton . . . . .	403
7.3.2	Intervalley Scattering of a Direct Exciton . . . . .	411
7.4	Excitons and Induced Self-Trapping in Mixed Crystals of Thallous Halides . . . . .	412
7.4.1	Exciton States in a Mixed Crystal . . . . .	412
7.4.2	Self-Trapping Induced by Alloying . . . . .	418
7.5	Excitons in Thallous Halides in External Fields . . . . .	422
7.5.1	Magnetic Field . . . . .	422
7.5.2	Electric Field . . . . .	432
7.5.3	Uniaxial Stress Field . . . . .	435
8.	<b>Photocarrier Motion in Ionic Crystals . . . . .</b>	<b>437</b>
8.1	Photocurrent and Measurement . . . . .	438
8.1.1	Photocurrent . . . . .	438
8.1.2	Blocking Electrode Method and Response . . . . .	439
8.1.3	Spectral Dependence of Photoconductivity . . . . .	442
8.2	Measurements of Carrier Mobility and Cyclotron Resonance in Insulating Photoconductors . . . . .	444
8.2.1	Carrier Mobility . . . . .	444
8.2.2	Drift Mobility Measurement . . . . .	447
8.2.3	Hall and Magnetoresistance Mobility Measurements . . . . .	447
8.2.4	Detection of Cyclotron Resonance . . . . .	450
8.3	Polaron and Mobility . . . . .	451
8.3.1	Polaron Masses and Coupling Constants . . . . .	451
8.3.2	Polaron Mobilities . . . . .	452
8.4	Magnetoconductivity . . . . .	461
8.4.1	Spin-Dependent Magnetoconductivity . . . . .	461
8.4.2	Photomagnetocurrent . . . . .	464
8.5	Polarons with High Energy . . . . .	468
8.5.1	Nonparabolicity of the Polaron Energy Spectrum . . . . .	468
8.5.2	Hot-Polaron Transport Phenomena . . . . .	470
9.	<b>Excitons and Phonon Couplings in Quasi-One-Dimensional Crystals . . . . .</b>	<b>475</b>
9.1	Halogen-Bridged Mixed-Valence Chain Compounds . . . . .	476
9.2	Polyacetylene . . . . .	482

**XII      Contents**

9.3 Mixed Stacked Donor-Acceptor Charge Transfer Complexes . . .	489
9.4 Segregated Stacked Donor-Acceptor Charge Transfer Complexes	495
<b>References . . . . .</b>	<b>499</b>
<b>Subject Index . . . . .</b>	<b>521</b>