60 Springer Series in Solid-State Sciences

Edited by Peter Fulde

Springer Series in Solid-State Sciences

Editors: M. Cardona P. Fulde K. von Klitzing H.-J. Queisser

40 **Semiconductor Physics** An Introduction 3rd Edition By K. Seeger

41 **The LMTO Method** Muffin-Tin Orbitals and Electronic Structure By H. L. Skriver

42 **Crystal Optics with Spatial Dispersion, and Excitons** By V. M. Agranovich and V. L. Ginzburg

43 **Resonant Nonlinear Interactions of Light with Matter** By V. S. Butylkin, A. E. Kaplan, Yu. G. Khronopulo, and E. I. Yakubovich

44 **Elastic Media with Microstructure II** Three-Dimensional Models By I. A. Kunin

45 **Electronic Properties of Doped Semiconductors** By B. I. Shklovskii and A. L. Efros

46 **Topological Disorder in Condensed Matter** Editors: F. Yonezawa and T. Ninomiya

47 **Statics and Dynamics of Nonlinear Systems** Editors: G. Benedek, H. Bilz, and R. Zeyher

48 **Magnetic Phase Transitions** Editors: M. Ausloos and R. J. Elliott

49 **Organic Molecular Aggregates,** Electronic Excitation and Interaction Processes Editors: P. Reineker, H. Haken, and H. C. Wolf

50 **Multiple Diffraction of X-Rays in Crystals** By Shih-Lin Chang

51 **Phonon Scattering in Condensed Matter** Editors: W. Eisenmenger, K. Laßmann, and S. Döttinger

52 **Superconductivity in Magnetic and Exotic Materials** Editors: T. Matsubara and A. Kotani

53 **Two-Dimensional Systems, Heterostructures, and Superlattices** Editors: G. Bauer, F. Kuchar, and H. Heinrich

54 **Magnetic Excitations and Fluctuations** Editors: S. Lovesey, U. Balucani, F. Borsa, and V. Tognetti

55 **The Theory of Magnetism II** Thermodynamics and Statistical Mechanics By D. C. Mattis

56 **Spin Fluctuations in Itinerant Electron Magnetism** By T. Moriya

57 **Polycrystalline Semiconductors,** Physical Properties and Applications Editor: G. Harbeke

58 **The Recursion Method and Its Applications** Editors: D. Pettifor and D. Weaire

59 **Dynamical Processes and Ordering on Solid Surfaces** Editors: A. Yoshimori and M. Tsukada

60 **Excitonic Processes in Solids** By M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura

61 **Localization, Interaction, and Transport Phenomena** Editors: B. Kramer, G. Bergmann, and Y. Bruynseraede

62 **Theory of Heavy Fermions and Valence Fluctuations** Editors: T. Kasuya and T. Saso

63 **Electronic Properties of Polymers and Related Compounds** Editors: H. Kuzmany, M. Mehring, and S. Roth

64 **Symmetries in Physics, Group Theory Applied to Physical Problems** By W. Ludwig

65 **Phonons: Theory and Experiments II** By P. Brüesch

Volume 1-39 are listed on the back inside cover

Excitonic Processes in Solids

By M. Ueta, H. Kanzaki, K. Kobayashi,
Y. Toyozawa, and E. Hanamura

With 307 Figures

Springer-Verlag
Berlin Heidelberg New York Tokyo

Professor Dr. Masayasu Ueta

Department of Physics, Tohoku University, Sendai 980, Japan
Present address: Department of Physics, Kyoto Sangyo University, Kyoto 603, Japan

Professor Dr. Hiroshi Kanzaki*
Professor Dr. Koichi Kobayashi**
Professor Dr. Yutaka Toyozawa

Institute for Solid State Physics, University of Tokyo, Minato-ku, Tokyo 106, Japan
* Present address: Fuji Film Research Lab., Minami-Ashigara, Kanagawa 250-01, Japan
** Present address: College of Liberal Arts, Toyama University, Toyama 930, Japan

Professor Dr. Eiichi Hanamura

Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Series Editors:
Professor Dr., Dr. h. c. Manuel Cardona
Professor Dr., Dr. h. c. Peter Fulde
Professor Dr. Klaus von Klitzing
Professor Dr. Hans-Joachim Queisser

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

ISBN-13:978-3-642-82604-7 e-ISBN-13:978-3-642-82602-3
DOI: 10.1007/978-3-642-82602-3

Library of Congress Cataloging-in-Publication Data. Main entry under title: Excitonic processes in solids. (Springer series in solid-state sciences; 60) Bibliography: p. Includes index. 1. Exciton theory. 2. Solids. I. Ueta, M. (Masayasu), 1919-. II. Series. QC176.8.E9E94 1985 530.4'1 85-27898

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, reuse 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 "Verwertungsgesellschaft Wort", Munich.

© Springer-Verlag Berlin Heidelberg 1986
Softcover reprint of the hardcover 1st edition 1986

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.

Typesetting: Schwetzinger Verlagsdruckerei, 6830 Schwetzingen

2153/3130-543210

Preface

An exciton is an electronic excitation wave consisting of an electron-hole pair which propagates in a nonmetallic solid. Since the pioneering research of Frenkel, Wannier and the Pohl group in the 1930s, a large number of experimental and theoretical studies have been made. Due to these investigations the exciton is now a well-established concept and the electronic structure has been clarified in great detail.

The next subjects for investigation are, naturally, dynamical processes of excitons such as excitation, relaxation, annihilation and molecule formation and, in fact, many interesting phenomena have been disclosed by recent works. These excitonic processes have been recognized to be quite important in solid-state physics because they involve a number of basic interactions between excitons and other elementary excitations. It is the aim of this quasi monograph to describe these excitonic processes from both theoretical and experimental points of view.

To discuss and illustrate the excitonic processes in solids, we take a few important and well-investigated insulating crystals as playgrounds for excitons on which they play in a manner characteristic of each material. The selection of the materials is made in such a way that they possess some unique properties of excitonic processes and are adequate to cover important interactions in which excitons are involved. In each material, excitonic processes are described in detail from the experimental side in order to show the whole story of excitons in a particular material. Part of this book is devoted to the theoretical description of the excitonic processes which play particularly important roles in the materials chosen in this book but are not necessarily restricted to these materials. The theory is presented in a general fashion so as to cover a variety of phenomena which have been of recent interest.

It should be remarked that, although this book has been written through the cooperation of five authors, the main contribution to Chap. 3 was made by Ueta, Chaps. 5 and 6 by Kanzaki, Chaps. 7, 8, and 9 by Kobayashi, Chaps. 1 and 4 by Toyozawa and Chap. 2 by Hanamura.

The authors wish to express their gratitude to all of their colleagues for collaboration and discussions at various stages of their researches on excitons. One of the authors (MU) would like to acknowledge the assistance of Prof. T. Itoh and Dr. Y. Nozue in completing the manuscript. The authors thank the original authors of the figures used in this book who kindly gave permission to reproduce them. Thanks are also due to the Physical Society of Japan, The American Physical Society, The Institute of Physics, Progress of Theoretical

Physics, Akademie-Verlag, International Union of Crystallography, North-Holland Publishing Company, Pergamon Press Ltd. and Plenum Press for granting them permission for the reproduction of the figures. The authors are grateful to Miss Chikako Okada, Miss Takako Tokanai, Miss Yoko Kobayashi and Dr. Atsuko Sumi for typing the manuscript. Finally the authors should like to acknowledge the constant help and encouragement furnished by their wives, Chisako Ueta, Kiyo Kanzaki, Rei Kobayashi, Asako Toyozawa and Toshiko Hanamura without whose aid the work on excitons, on which this book is based, would probably not have been done.

Tokyo and Sendai 1984

M. Ueta, H. Kanzaki, K. Kobayashi,
Y. Toyozawa, E. Hanamura

Contents

1. Introduction 1

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

2. Theoretical Aspects of Excitonic Molecules 20

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 – TlX 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_2O 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

3. The Exciton and Excitonic Molecule in Cuprous Halides 116
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 Molcecule 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

4. Theory of Excitons in Phonon Fields 203
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 *t-U-S* 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

5. Excitons in Condensed Rare Gases 285
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

6. Exciton-Phonon Processes in Silver Halides 309
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

7. Excitons and Their Interactions with Phonons and External Fields in Thallous Halides 370
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. Photocarrier Motion in Ionic Crystals 437
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. Excitons and Phonon Couplings in Quasi-One-Dimensional Crystals . . 475
9.1 Halogen-Bridged Mixed-Valence Chain Compounds 476
9.2 Polyacetylene 482

9.3 Mixed Stacked Donor-Acceptor Charge Transfer Complexes . . . 489
9.4 Segregated Stacked Donor-Acceptor Charge Transfer Complexes 495

References 499

Subject Index 521