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K.S. Song R.T. Williams

Self-Trapped Excitons

With a Foreword by Y. Toyozawa

With 219 Figures

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Foreword

The optical excitation of molecules and condensed matter results in a sudden change of electronic charge distribution, thereby destroying the balance of electron-mediated interatomic forces which governed the ground electronic state.

To pursue how the atoms move after the optical excitation and to see which positions they finally take after relaxation is not only interesting in itself but also reveals the nature of the interatomic forces which was concealed in the ground state behind the silent balance. The study of the “relaxed excited states” will thus provide us with a better and deeper understanding of the ground state.

The last statement has been obvious for molecules of finite size, but not necessarily so for solids with translational symmetry in which the electronic excitation—exciton—is usually extended over the entire lattice so that the vibronic or electron—lattice interaction is diluted to insignificance. However, since Landau’s prediction in 1933, it has gradually been realized experimentally and theoretically that the electrons, holes, and excitons in quite a number of insulators become stabilized by self-trapping, namely by localizing themselves in the potential well due to the self-induced lattice distortion. The history of this realization, however, has not been straightforward. One reason was that the self-trapped state with broken translational symmetry is a notion which, strictly speaking, is valid only in the adiabatic limit. The early studies concentrated on electrons or holes interacting with the displacement polarization of the ionic lattice, in which case the nonadiabatic “polaron” state dominates. The self-trapped state and the free state coexist as distinguishable states when they are two minima of the adiabatic potential with a significant barrier between them. This is the case with excitons in a three-dimensional lattice. While the excitons immediately after the optical creation are in the free state, the self-trapped state can be reached, by tunneling through the potential barrier at low temperatures, only when it is energetically more stable than the former; namely, in those materials with exciton—lattice interaction larger than a certain critical value. In most narrow gap insulators which have long been the favorite objects of semiconductor physicists, the exciton—lattice interaction is below that critical value—another reason that the self-trapping was considered an abnormal or exceptional situation. In moderate or large gap insulators, however, self-trapping is rather more normal than exceptional. It is in these materials that the optical excitation of the electronic system causes a variety of dramatic changes

in the local atomic arrangements, including the defect formations which are hardly imaginable within a simple extrapolation from semiconductors.

An immense quantity of knowledge on self-trapped excitons in a variety of materials has been accumulated over the past thirty years. The most exciting topic in the recent developments is perhaps the parity breaking of the self-trapped exciton in contradistinction to the parity conserving self-trapped hole in alkali halides, as revealed by a number of experimental and theoretical studies.

It is most welcome to the community of condensed matter and molecular science that Dr. Augustin K.S. Song and Dr. Richard T. Williams, who played the key roles in promoting as well as confirming the parity breaking, collaborated to write a book on Self-Trapped Excitons. In this book one finds a comprehensive review of recent studies on self-trapped excitons in typical materials such as condensed rare gases, alkali halides, silver halides, silicon dioxide, arsenic chalcogenides, organic molecular crystals, and low-dimensional crystals. The defect formation is discussed in the same context with the self-trapping. Theoretical explanations as well as experimental descriptions are elaborate and lucid. The readers will find inexhaustible interest in the varying interplay of the electronic states and the atomic motions which depends on the nature of the interatomic bonds and hence on the species of the materials. Needless to say, the book will continue to serve as the most up-to-date reliable reference on self-trapped excitons until the next burst of developments which will be brought about by younger generations who are inspired by this book.

Tokyo, July 1992

Yutaka Toyozawa

Preface

Excitons are delocalized carriers of electronic excitation energy in nonmetallic crystals. Self-trapping of an exciton concentrates that energy to atomic dimensions and thus strongly influences the transport and disposition of electronic energy in materials susceptible to this instability of the excited state. Self-trapped excitons are of fundamental importance for atomic processes induced by electronic excitation in pure insulators, including photochemical defect formation and some forms of desorption from surfaces, as well as electronic processes of energy transport, luminescence, and the spectrum of fundamental edge absorption. Self-trapped excitons (STEs) can be found in a wide variety of halide crystals, condensed rare gases, organic molecular crystals, some oxides and other chalcogenides, a few semiconductor alloys, and quasi-one-dimensional materials. An interesting class of defect states in semiconductors and insulators appears best described in terms of extrinsic self-trapping of electrons or excitons. Certain phase transitions in low-dimensional materials have been discussed in terms of spontaneous generation of STEs in the ground state. Aside from its relevance to such topics, the self-trapped exciton is a fascinating opportunity to study defect physics in the excited state of a perfect crystal. It is challenging to the theorist who studies excited states in solids and explores the variety of relaxed configurations that an unstable lattice may take, and to the experimentalist who adapts defect spectroscopies previously conducted on stable ground state species to dynamic processes occurring as fast as a few hundred femtoseconds.

In the present volume, an up-to-date understanding of the structure and properties of the STE in several groups of materials is presented based on theoretical and experimental works of recent years. Self-trapped excitons will be treated theoretically as localized excited states in a deformable crystal, using self-consistent methods developed originally for defects in solids. By allowing the involved ions to relax as the electronic and lattice energies are minimized together, insight on STE structure, dynamics, and evolution of lattice defects can be gained. Complementing this theoretical approach, we review a comprehensive array of experimental data with emphasis on excited-state spectroscopies, since the STE is after all a transient “defect” state that will generally revert to the perfect crystal in the electronic ground state. Ultrafast spectroscopy, optically detected magnetic resonance, two-step excitation techniques, and methods using synchrotron radiation are among the spectroscopies employed to study exciton self-trapping and defect formation. We have attempted to survey the widest

possible range of materials in which exciton self-trapping has been established with confidence. We have addressed rare gas solids, alkaline earth fluorides, alkali halides, silicon dioxide, organic molecular crystals, silver halides, chalcogenide crystals and glasses, alkaline-earth fluorohalides, alkali silver halides, and low-dimensional systems. On studying seemingly disparate materials together, we find several consistent themes which underlie the basic physics of the self-trapped excitons. These deal with the way the excited electronic system in an insulator interacts with the lattice prior to its return (radiatively or non-radiatively) to the ground state of the crystal, or its evolution to permanent lattice defects.

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K.S. Song
R.T. Williams

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