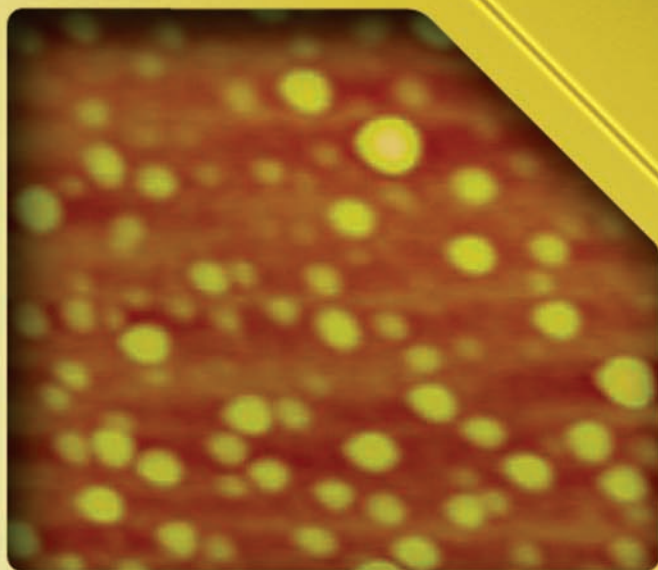


Edited by **Cole W. Litton,**  
**Donald C. Reynolds, Thomas C. Collins**

# Zinc Oxide Materials

for Electronic and  
Optoelectronic Device  
Applications



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# **Zinc Oxide Materials for Electronic and Optoelectronic Device Applications**

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# Zinc Oxide Materials for Electronic and Optoelectronic Device Applications

Edited by

COLE W. LITTON

*Air Force Research Laboratory, Ohio, USA*

DONALD C. REYNOLDS

*Wright State University, Ohio, USA*

THOMAS C. COLLINS

*Oklahoma State University, Oklahoma, USA*



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*This book is dedicated to the memory of Cole W. Litton who was  
the driving force behind it and the lead editor. Cole passed  
away before its completion.*

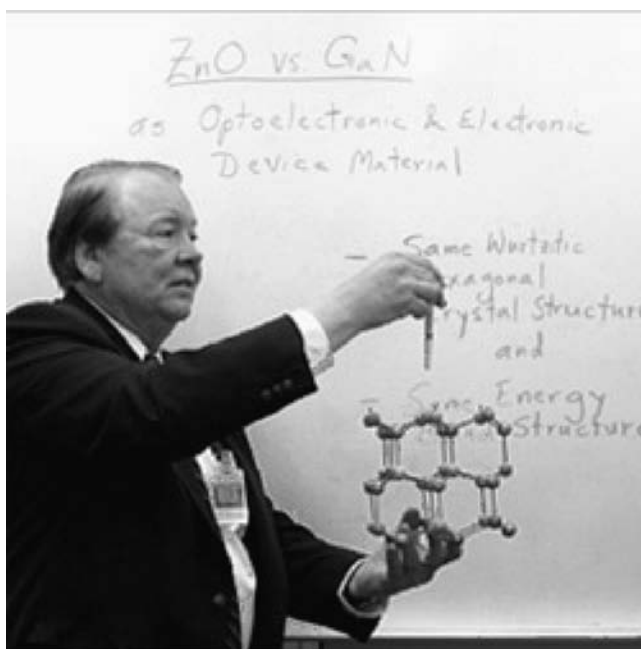




# In Memoriam: Cole Litton

Cole W. Litton, the editor and compiler of *Zinc Oxide Materials for Electronic and Optoelectronic Device Applications*, died of a heart attack on Tuesday, January 26, 2010, while attending the SPIE Photonics West Conference in San Francisco.

Cole was a native of Memphis, Tennessee, born in 1930, and he attended the University of Tennessee graduating with a bachelor's degree. He served for four years as an officer in the US Air Force and then joined the Air Force Research Laboratory as a civilian scientist at Wright Patterson Air Force Base in Dayton, Ohio. There he worked on the solid-state physics team of Don Reynolds, Tom Collins, and later David Look, and was the principal designer of what became the world's highest resolution optical spectrometer. He spent 50 years with the Air Force during which time he studied at several other universities in the United States and Europe. Litton was acknowledged as a world leader in research in solid-state and semiconductor physics and crystal growth, particularly in the optical, electrical, and structural properties of compound semiconductor materials and devices. In 1971 Cole was elected a fellow of the American



Physical Society. He has been a long-time devoted member of SPIE, where he was a founder and current co-chair of the Gallium Nitride Materials and Devices Conference and also the Oxide-Based Materials and Devices Conference, two of the most successful conferences at Photonics West since their inception. In memory of Litton, the Gallium Nitride Materials and Devices Conference will now bear his name, recognizing his many contributions not only to SPIE but to advancing optics- and photonics-based research as well.

Cole Litton retired in 2006 as Senior Scientist from the Air Force Research Laboratory, but he continued to enjoy an active role in scientific workshops and symposia. At the time of his death, he had authored or co-authored about 200 scientific/technical research papers published in physics and engineering journals. He was committed to discovery and was passionate about the future of science and technology. Cole died fully engaged in the activity he most enjoyed: participating in scientific meetings. He was a unique individual with a great love of life, and he will be remembered by all who knew him.

David F. Bliss  
US Air Force Laboratory  
Hanscom Research Site  
MA, USA

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# Series Preface

## WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, and so on, all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure–property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

Peter Capper  
Safa Kasap  
Arthur Willoughby



# Preface

Zinc oxide (ZnO) powder has been widely used as a major white paint pigment and industrial processing chemical for nearly 150 years. Indeed, interest in this fascinating chemical compound dates back even to antiquity. ZnO, the first man-made zinc compound, originated many centuries ago as an impure by-product of copper smelting. The ancients discovered and put to use some of its unusual properties, which included production of the first brass metal, development of a purified ZnO for medical purposes, and the early alchemists even attempted to make gold with it. Beginning in the early 1900s, white, polycrystalline ZnO powder found extensive application in medical technology, in particular the cosmetics and pharmaceutical industries, where it is today used in facial and body powders, sun screen preparation, antibiotic lotions and salves and in dental technology for dental cements.

A modern rediscovery of ZnO and its potential applications began in the mid 1950s. At that time, science and industry alike, mostly in the US and Europe, began to realize that ZnO had many interesting novel properties that were worthy of further investigation and exploration. These novel properties included its semiconductor, piezoelectric, luminescent, ultraviolet (UV) absorption, catalytic, ferrite, photoconductive and photochemical properties. Although study of the photoluminescence and electroluminescence properties of ZnO began as early as the mid 1930s, extensive investigation of its semiconductor properties did not begin until the mid to late 1950s, once good single crystals became available, either from natural sources, or grown synthetically by vapor transport and various other techniques, for study of the optical, electrical and structural properties of semiconducting ZnO. These early ZnO single crystals, mostly needles, platelets and prisms, were, however, small and limited in size to a few millimeters. ZnO single crystals typically crystallize in the wurtzitic, hexagonal modification, are visibly transparent and have a wide, direct band gap in the near UV at 3.437 eV (at 2 K). During this same period, the late 1950s to early 1960s, it was also recognized that ZnO had very high piezoelectric coefficients which led to the development of ZnO-based piezoelectric transducers, such as sensitive strain gauges and pressure sensors, a technology which continues today. Throughout the 1960s, extensive investigations of the fundamental semiconductor properties of ZnO were made, including study of its energy band structure, band gaps, excitonic properties, electron and hole effective masses, phonon properties and the electrical transport properties of the intrinsic (undoped) material. At this time (the mid to late 1960s) it was also recognized that ZnO, like the other wide band gap II–VI materials, would be difficult to dope controllably with high concentrations of shallow donor and acceptor impurities in order to demonstrate n- and p-type conductivity and p-n junctions, which would be necessary in order to realize the full potential of ZnO in devices, such as UV diode emitters, detectors and transistors. At that time, modern epitaxial growth and doping techniques, such as molecular beam epitaxy (MBE) and metal organic chemical

vapor deposition (MOCVD), had not yet been developed, and p-type doping of both epitaxial films and bulk substrates did not exist; moreover, lack of large, bulk single crystals of ZnO also hampered progress in the development of ZnO-based electronic and optoelectronic devices. Nevertheless, much progress has been made over the past four decades (1970 to present) on the development of ZnO-based transducers, varistors, white-light-emitting cathodoluminescent phosphors (in conjunction with ZnS), optically transparent electrically conducting films, optically pumped lasing, MSM-type UV detectors, based on both ZnO (near UV) and MgZnO/ZnO heterostructures (deeper UV), and surface acoustic wave devices, none of which require the use of p-type ZnO.

Demonstration of the first InGaN/GaN-based, long-lived, room-temperature, continuous wave (CW) blue light-emitting diodes (LEDs) and diode lasers in Japan in the mid 1990s, led several ZnO investigators to consider the possibility of using isomorphic, nearly lattice-matched, c-plane bulk ZnO as a substrate for GaN device epitaxy ( $\sim 2\%$  mismatch to GaN), since bulk GaN substrates did not exist, and it was clear that the large threading dislocations resulting from growth of InGaN/GaN laser device structures on lattice mismatched c-plane sapphire ( $\sim 14\%$  lattice mismatch) were degrading both the performance and lifetimes of the blue laser diodes, particularly in CW, single mode operation. Earlier a US nitride research group had already demonstrated that GaN device epitaxy could be grown by MBE on small, c-plane ZnO substrates with as much as two to three orders of magnitude reduction in threading dislocation densities within the GaN device epitaxy, in comparison with growth on highly lattice mismatched sapphire substrates. Over the past decade, this achievement led another group to successfully grow and market large (40 mm diameter), high-quality, single-crystal ZnO substrates by vapor transport techniques specifically for this purpose and more recently still another group has also developed large diameter, bulk ZnO substrates by the Pressure-Melt technique for this purpose. Work is presently underway to demonstrate the MBE growth of AlGaN/GaN-based microwave power field-effect transistor (FET) device structures, where the relatively cheap ZnO substrate will be etched away and a high thermal conductivity substrate substituted by wafer bonding techniques to improve heat dissipation from the device.

Over the past decade, a number of groups have proposed that ZnO might be a good optoelectronic device material in its own right, owing to the many similarities between the optical, electrical and structural properties of ZnO and GaN, including their band gaps (3.437 eV for ZnO and 3.50 eV for GaN at 2 K) and their lattice constants. In addition, still others have noted that ZnO has a free exciton binding energy of 60 meV, approximately twice that of GaN, which could lead to highly efficient, ZnO- and MgZnO-based, UV injection lasers (UV laser diodes and detectors) at room temperature, provided that efficient p-doping and good p-n junctions and heterojunctions can be demonstrated in these materials. p-type doping of hetero-epitaxial ZnO on sapphire has been reported by several Japanese and US groups, using N acceptor doping and several different growth techniques, with varying degrees of success, but a major breakthrough was achieved by a US group recently which reported the first MBE growth of homo-epitaxial, N-doped, p-type ZnO on high-resistivity, Li-diffused ZnO substrates. Although the temperature-dependent Hall conductivity of these p-type layers is not yet fully understood, this approach could lead rapidly to p-doping at higher hole mobilities and carrier concentration and to the formation of good p-n junctions, provided that we can achieve a better understanding of both the shallow and deep donor/acceptor compensation mechanisms

in ZnO. It is important to address the questions of donor and acceptor impurity incorporation together with the likely formation of native point defect donors and acceptors in ZnO and their possible compensation mechanisms; and look into the question of possible hydrogen donor incorporation in ZnO which must be better understood if rapid progress is to be made in the p-doping of ZnO.

This book comprises some 12 chapters that are written by experts in various aspects of ZnO materials and device technology. The topics included and discussed in these chapters range from our latest understanding of the energy band structure and spintronics (Chapter 1) to our most recent understanding of the fundamental optical and electrical properties of ZnO (Chapters 2 and 3). With the generation of new devices, one has to understand and control the electronic contacts of ZnO. This is covered in Chapter 4. The latest advances in our understanding of the formation of native point defect donors and acceptors in ZnO are discussed and summarized in Chapter 5. The following chapter (Chapter 6) investigates both the intrinsic and extrinsic defects that are found in ZnO. The growth of the ZnO crystals and substrates are discussed in the next three chapters (Chapters 7, 8 and 9) along with hybrid devices, Chapter 10 reports on some recent advances in optically pumped lasing and room temperature stimulated emission from ZnO-based materials. Chapter 11 reviews the progress of UV photodetectors and points out the promise for unique applications such as single-photon detection. The final chapter (Chapter 12) presents a review of optical properties of ZnO quantum wells in which strong stimulation was observed in ZnO/ZnMgO multiple quantum wells from 5 °C to room temperature.

Cole W. Litton  
Donald C. Reynolds  
Thomas C. Collins



# List of Contributors

**M. N. Alexander**, Air Force Research Laboratory, Hanscom AFB, MA, USA

**D. M. Bagnall**, University of Southampton, Southampton, UK

**Leonard J. Brillson**, The Ohio State University, Columbus, OH, USA

**M. J. Callahan**, Teleos Solar, Hanson, MA, USA and Air Force Research Laboratory, Hanscom AFB, MA, USA

**Gene Cantwell**, ZN Technology, Inc., Brea, CA, USA

**B. Claffin**, Wright State University, Dayton, OH, USA

**T. C. Collins**, Oklahoma State University, Stillwater, OK, USA

**Dirk Ehrentraut**, Tohoku University, Aoba-ku, Sendai, Japan

**R. J. Hauenstein**, Oklahoma State University, Stillwater, OK, USA

**A. Hoffmann**, Technical University Berlin, Berlin, Germany

**D. M. Hofmann**, Justus Liebig University Giessen, Giessen, Germany

**Anderson Janotti**, University of California, Santa Barbara, CA, USA

**Masashi Kawasaki**, Tohoku University, Sendai, Japan, Cross-Related Materials Research Group, Advanced Science Institute, RIKEN, Wako, Japan and CREST, Japan Science and Technology Agency, Tokyo, Japan

**Hideomi Koinuma**, The University of Tokyo, Kashiwa, Chiba, Japan

**C. W. Litton**, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, USA

**D. C. Look**, Wright State University, Dayton, OH, USA

**Yicheng Lu**, Rutgers University, Piscataway, NJ, USA

**Takayuki Makino**, Tohoku University, Sendai, Japan

**B. K. Meyer**, Justus Liebig University Giessen, Giessen, Germany

**Hadis Morkoç**, Virginia Commonwealth University, Richmond, VA, USA

**D. C. Reynolds**, Wright State University, Dayton, OH, USA and Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, USA

**Yusaburo Segawa**, Advanced Science Institute, RIKEN, Wako, Japan

**Ryoko Shimada**, Virginia Commonwealth University, Richmond, VA, USA

**J. J. Song**, ZN Technology, Inc., Brea, CA, USA and University of California at San Diego, La Jolla, CA, USA

**J. Stehr**, Justus Liebig University Giessen, Giessen, Germany

**Chris G. Van de Walle**, University of California, Santa Barbara, CA, USA

**Buguo Wang**, Solid State Scientific Inc., Nashua, NH, USA

**Jizhi Zhang**, ZN Technology, Inc., Brea, CA, USA

**Jian Zhong**, Rutgers University, Piscataway, NJ, USA



# 1

## Fundamental Properties of ZnO

*T. C. Collins and R. J. Hauenstein*

*Department of Physics, Oklahoma State University, Stillwater, OK, USA*

### 1.1 Introduction

#### 1.1.1 Overview

Wurtzitic ZnO is a wide band gap semiconductor ( $E_g = 3.437$  eV at 2 K) that has many applications, including piezoelectric transducers, varistors, phosphors, and transparent conduction films. Most of these applications only require polycrystalline materials; however, recent successes in producing large-area single crystals make possible the production of blue and UV light emitters and high temperature, high power transistors. The main advantage of ZnO as a light emitter is its large exciton binding energy ( $E_b = 60$  meV). This binding energy is three times larger than that of the 20 meV exciton of GaN, which permits excitonic recombination to dominate in ZnO at room temperature (and even above). Excitonic recombination is preferable because the exciton, being an already bound system, radiatively recombines with high efficiency without requiring traps to localize carriers, as in the case in radiative recombination of electron–hole plasmas. Secondly, the deeper exciton of ZnO is more stable against field ionization due to piezoelectrically induced fields. Such piezoelectric effects are expected to increase with increasing dopant concentration for both ZnO and GaN.

For electronic applications, the attractiveness of ZnO lies in having high breakdown strength and high saturation velocity. ZnO also affords superior radiation hardness compared with other common semiconductor materials, such as Si, GaAs, CdS, and even GaN, enhancing the usefulness of ZnO for space applications. Optically pumped UV laser action in ZnO has already been demonstrated at both low and high temperatures

although efficient electrically induced lasing awaits further improvements in the experimental ability to grow high quality p-type ZnO material. Nonetheless, over the past decade, researchers world-wide have made substantial theoretical and experimental progress concerning the p-type dopability of ZnO, with  $10^{17} \text{ cm}^{-3}$  range hole concentrations now plausibly achieved with material stability persisting for over 1 year, and with isolated (though often controversial) reports of hole concentrations as high as  $\sim 10^{19} \text{ cm}^{-3}$  even being reported from time to time. Finally, ZnO structures can be doped with transition metal (TM) ions to form dilute magnetic materials, denoted (Zn,TM)O, which can form a ferromagnetic state, an antiferromagnetic state as well as a general spin glass. The important point is that the Curie temperature ( $T_C$ ) can be *above* room temperature. Such above-room-temperature anti- and ferromagnetic states form the basis for novel charge-based, spin-based, or even mixed spin- and charge-based devices which, collectively, are known as “spintronic” devices.

### 1.1.2 Organization of Chapter

The remainder of this chapter is organized as follows. In Section 1.2, a theoretical overview of the fundamental band structure of ZnO near the zone center is presented. The discussion includes the long-standing controversy over the symmetry-ordering of the valence bands at the  $\Gamma$  point. Next, in Section 1.3, the optical properties of intrinsic ZnO are reviewed, with particular emphasis on the excitons. Also presented in this same section are a discussion of the interaction of light, magnetic field, and strain field, as three examples of the general types of calculations done for excitons in ZnO, as well as a discussion of spatial resonance dispersion (Section 1.3.4) in which the polariton, a combined state arising out of the mixing of an exciton and light, plays a particularly important role. The electrical properties of ZnO are considered next in Section 1.4, including a discussion of intrinsic along with n-type and p-type ZnO. In particular, the important question of p-type dopability is discussed in detail in Section 1.4.3. For the implementation of optoelectronic devices, one will need Schottky barriers and ohmic contacts; recent progress in these areas is presented in Section 1.4.4. For heterojunction-based devices, band gap engineering will be required and this is considered in Section 1.5. Finally, presented in Section 1.6 is the theoretical basis for the ZnO spintronic device. The different models are based on the Heisenberg Spin Hamiltonian to describe the dilute magnetic system (Zn,TM)O. One can investigate both the interaction of the carriers with the magnetic moment of the TM as well as the TM–TM interactions. It is found that the resulting Curie temperature can be above room temperature. Spintronic devices made of (Zn,TM)O are expected to be faster and to consume less power since flipping the spin requires 10–50 times less power, and occurs roughly an order of magnitude faster, than does transporting an electron through the channel of traditional field-effect transistors (FETs).

## 1.2 Band Structure

### 1.2.1 Valence and Conduction Bands

The general electronic structure of binary III–V and II–VI compounds form semiconductors with the valence band mostly derived from the covalent bonding orbitals (s and p).

While the conduction band consists of antibonding orbitals, as one moves further outward from column IV of the periodic table, the binary compound semiconductors acquire a more ionic character. These compounds form cubic (zinc blende) and hexagonal (wurtzite) crystal structures, with ZnO crystallized in the wurtzite structure. The difference between the zinc blende and wurtzite structures is that the zinc blende is cubic while the wurtzite is a distortion of the cube in the [111] direction generally taken to be the z direction in the wurtzite.

The ionicity effect puts more electrons on the group V or group VI atoms giving the charge density more s and p characteristics of these elements in the valence band. It also causes gaps at the edge of the Brillouin zone compared with just covalent bonding materials. This translates into flatter bands across the Brillouin zone.

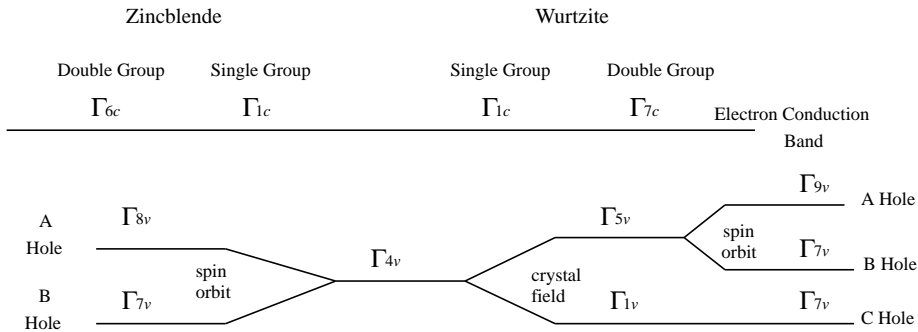
ZnO is a direct band gap semiconductor with valence-band maximum and conduction-band minimum occurring at the  $\Gamma$  point. The conduction band is s-like from Zn at  $\Gamma$  and is spin degenerate. The top three valence bands are p-like in character. They are split by the spin-orbit interaction in both the zinc blende and wurtzite symmetry, while wurtzite symmetry also has a crystal field splitting.

Figure 1.1 shows<sup>[1]</sup> the Quasi-cubic model<sup>[2-4]</sup> of the bottom of the conduction band and the top of the valence band. Assuming that one has both zinc blende and wurtzite and that  $\mathcal{H}_{so} = \Delta \mathbf{L} \cdot \mathbf{S}$ , one can write matrices of the form:

$$\begin{pmatrix} \Delta & 0 & 0 \\ 0 & \Delta & 0 \\ 0 & 0 & -2\Delta \end{pmatrix} \tag{1.1}$$

for zinc blende, using  $j = 3/2$  and  $j = 1/2$  eigenstates. For wurtzite the basis is rotated as stated above, so that one has  $S_{+\alpha}, S_{-\beta}, -S_{-\alpha}, S_{+\beta}, S_{z\alpha},$  and  $S_{z\beta}$ . This basis gives matrices (including crystal field effects  $\delta$ ) of the form

$$\begin{pmatrix} \Delta & 0 & 0 \\ 0 & -\Delta & -i\sqrt{2}\Delta \\ 0 & i\sqrt{2}\Delta & -\delta \end{pmatrix}. \tag{1.2}$$



**Figure 1.1** Structure and symmetries of the lowest conduction band and upmost valence bands in ZnO compounds at the  $\Gamma$  point

#### 4 Fundamental Properties of ZnO

Using the values obtained by Thomas,<sup>[5]</sup> a difficulty arises. As can be seen in Equation (1.3), there are values of energy difference which can give a complex number for  $\delta$ :

$$\delta = \frac{1}{2}(2E_1 + E_2) + \frac{1}{2}\sqrt{E_2^2 - 2E_1(E_1 + E_2)} \quad (1.3)$$

where  $E_1$  is the energy difference between the  $\Gamma_9$  excitons and  $\Gamma_7$  exciton and  $E_2$  is the energy difference between the two  $\Gamma_7$  excitons. In fact, using Thomas<sup>[5]</sup> numbers,  $\delta$  is a complex number with  $\Gamma_9$  being the top valence band. This difficulty can be surmounted by assuming a negative spin-orbit splitting, which is different from all the other II–VI compounds and GaN. The physical mechanism that could produce a negative spin-orbit splitting was investigated by Cardona<sup>[6]</sup> for CuCl. In this zinc blende material, it was postulated that the valence band was formed from Cl wave functions, with a large proportion of Cu wave functions (Cu 4s3d). The inverted nature of the CuCl indicates that the Cu contributes a negative term to the spin-orbit splitting, since for this material the anion splitting is small and negative. Cardona<sup>6</sup> estimated the “fraction” of the metal wave function in the valence band states by writing the spin-orbit splitting of the compound as:

$$\Delta = \frac{3}{2}[\alpha\Delta_{\text{hal}} - (1-\alpha)\Delta_{\text{met}}], \quad (1.4)$$

where  $\alpha$  is the proportion of halogen in the wave function,  $\Delta_{\text{hal}}$  is the one-electron atomic spin-orbit splitting parameter of the halogen and  $\Delta_{\text{met}}$  is one of the d-electrons of the metal. This gave  $\alpha = 0.25$  for CuCl. It was also presented that the energy interval between the ground state of the  $\text{Cu}^+$  ion ( $3d^{10}$ ) and the first excited state ( $3d^9, 4s$ ) is 2.75 eV.

Returning to ZnO, one finds the Zn d-bands below the uppermost p-like valence bands to be greater than 7 eV.<sup>[7–9]</sup> This makes it very unlikely that one has much mixing at all. Further, the d-band appeared to be relatively flat, noting again very little mixing. Also, the availability of ZnO crystals in which intrinsic exciton transitions<sup>[10]</sup> are observed in emission and their splitting in a magnetic field have led to a positive spin-orbit splitting of 16 meV. With this interpretation, the Quasi-cubic model<sup>[2–4]</sup> gives results in line with the other II–VI compounds.

In order to investigate the valence band ordering of ZnO further, Lambrecht *et al.*<sup>[11]</sup> calculated the band structure of ZnO using a linear muffin-tin potential and a Kohn–Sham local density approximation. The band gap at  $\Gamma$  was 1.8 eV compared with experiment of 3.4 eV and the Zn d-band was approximately 5 eV below the top of the valence band at  $\Gamma$ . To correct for the band gap Reynolds *et al.*<sup>[10]</sup> rigidly shifted the conduction band up to match the experimental  $\Gamma$ -point gap (a shift of 1.624 eV).

As is seen from above in the Quasi-cubic model,<sup>[2–4]</sup> the spin-orbit magnitude and sign are a function of the energy difference between the top of the valence and the 3d band of Zn. It is found to be greater than 7 eV.<sup>[7–9]</sup> In Reynolds *et al.*,<sup>[10]</sup> the d-band was adjusted to where the spin-orbit gave the right energy difference with the  $\Gamma_7$  above the  $\Gamma_9$ . The d band was put at 6.25 eV below the top of the valence band. This led to a negative  $g$ -value and of course a negative spin-orbit parameter. This in turn matched the experimental data given in Hong *et al.*<sup>[9]</sup> but with a different interpretation of the splitting of the exciton lines. Thus, there is no agreement of the spin-orbit value for ZnO. In first principle electron structure

calculations, one has an accuracy only on the order of  $\sim 100$  meV whereas the splittings of the levels in the top valence band are on the order of  $\sim 10$  meV!

### 1.3 Optical Properties

#### 1.3.1 Free and Bound Excitons

The optical absorption (emission) of electromagnetic radiation in a ZnO crystal is dependent on the matrix element

$$\int \Psi_f^* \mathcal{H}_{\text{int}} \Psi_i d\tau \quad (1.5)$$

where

$$\mathcal{H}_{\text{int}} = \frac{e\hbar}{imc} \mathbf{A} \cdot \nabla. \quad (1.6)$$

Here,  $\mathbf{A}$  is the vector potential of the radiation field and has the form

$$\mathbf{A} = \hat{n} |\mathbf{A}_0| e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)},$$

$e$  is the electronic charge,  $m$  is the electron mass,  $c$  is the velocity of light,  $\hat{n}$  is a unit vector in the direction of polarization, and  $\mathbf{q}$  is the wave vector. Expanding the spatial part of  $\mathbf{A}$  in a series gives

$$\mathcal{H}_{\text{int}} \equiv \sum_{j=0}^{\infty} \mathcal{H}_{\text{int}}^j \quad (1.7)$$

where

$$\mathcal{H}_{\text{int}}^j = (\mathbf{q} \cdot \mathbf{r})^j \hat{n} \cdot \nabla \quad (1.8)$$

and the dipole term is then the first term ( $i=0$ ). The matrix element in Equation (1.5) transforms under rotation like the triple direct product

$$\Gamma_f \otimes \Gamma_r^j \otimes \Gamma_i. \quad (1.9)$$

The selection rules are then determined by which of the triple-direct-product matrix elements in question do not vanish, where  $\Gamma_r^j$  is the symmetry of the expansion term  $\mathcal{H}_{\text{int}}^j$  in Equation (1.8).

The dipole moment operator for electric dipole radiation transforms like  $x$ ,  $y$ , or  $z$  dependent on the polarization. When the electric field vector  $\mathbf{E}$  of the incident light is parallel to the crystal axis of ZnO, the operator corresponds to the  $\Gamma_1$  representation. When it is perpendicular to the crystal axis, the operator corresponds to the  $\Gamma_5$  representation. Since the crystal has a principal axis, the crystal field removes part of the degeneracy of the p-levels as seen in Figure 1.1. Including spin in the problem doubles the number of levels. Since the conduction band at  $\mathbf{k}=0$  is the Zn (4s) level<sup>[4,5]</sup> it transforms as  $\Gamma_7$  while the  $\mathbf{k}=0$  at top of the valence band is made up of the O(2p) level and it splits into  $(p_x, p_y)\Gamma_5$

and  $(p_z)\Gamma_1$ . When crossed with the spin one has

$$\Gamma_5 \otimes D_{1/2} \rightarrow \Gamma_7 + \Gamma_9 \quad (1.10)$$

$$\Gamma_1 \otimes D_{1/2} \rightarrow \Gamma_7 \quad (1.11)$$

as shown in Figure 1.1.

One of the light absorption (emission) intrinsic states is an exciton, which is made up of a hole from the top of the valence band and an electron from the bottom of the conduction band. These are excitations of the  $N$ -particle system whereas electron structure calculations are of the  $(N \pm 1)$ -particle system. All solutions to the one-body calculations such as the one-particle Green's functions method do not contain the interaction of the excited "particle" with the other "particles." The more localized the excitation the more important it is to include this interaction. The more localized the excitation is, the flatter the one-electron bands, leading to heavier effective masses. This in turn leads to increased binding energy of the electron-hole pair. In ZnO, the binding energy of the ground state exciton is 60 meV. Adding in the Coulomb term of the electron-hole pair gives a hydrogenically bound pair. For the  $\Gamma_9$  hole and  $\Gamma_7$  electron one has

$$\Gamma_9 \otimes \Gamma_7 \rightarrow \Gamma_5 + \Gamma_6, \quad (1.12)$$

and for the  $\Gamma_7$  hole and  $\Gamma_7$  electron one has

$$\Gamma_7 \otimes \Gamma_7 \rightarrow \Gamma_5 + \Gamma_1 + \Gamma_2. \quad (1.13)$$

The  $\Gamma_5$  and  $\Gamma_6$  are doubly degenerate and the  $\Gamma_1$  and  $\Gamma_2$  are nondegenerate. The Hamiltonian for the exciton becomes:

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_h + \mathcal{H}_{\text{int}}, \quad (1.14)$$

where  $\mathcal{H}_e$  and  $\mathcal{H}_h$  are the Hamiltonian for the electron and the hole and  $\mathcal{H}_{\text{int}}$  is the interaction between the electron and hole including Coulomb, exchange and correlation. To first approximation one generally includes just the Coulomb term as noted above. Equation (1.14) gives what are referred to as the "free" excitons.

There are several extrinsic effects which modify the excitons. Most notable of these in ZnO are the bound complexes. One can have the exciton bound to an ionized donor or a neutral donor. In the case of the ionized donor, one has the molecular attraction of the exciton to the donor plus central cell corrections. For the neutral donor, one has again the molecular binding energy plus the ability of the neutral donor to be left in an excited state. Similar results are obtained with the ionized acceptor or neutral acceptor. The method of calculating these systems is to treat the system as a molecular system in the field of the crystal.

### 1.3.2 Effects of External Magnetic Field on ZnO Excitons

The case of an applied uniform magnetic field was developed by Wheeler and Dimmock<sup>[12]</sup> for the exciton in ZnO. It was assumed the electron bands are isotropic at least to second order in  $\mathbf{k}$  with only double spin degeneracy. The exciton equation is a simple