Unambiguous symmetry assignment for the top valence band of ZnO by magneto-optical studies of the free $A$-exciton state

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We studied the circular polarization and angular dependences of the magneto-photoluminescence spectra of the free $A$-exciton $1S$ state in wurtzite ZnO at $T = 5$ K. The circular polarization properties of the spectra clearly indicate that the top valence band has $\Gamma_7$ symmetry. The out-of-plane component $B_{\perp c}$ of the magnetic field, which is parallel to the sample’s c axis, leads to linear Zeeman splitting of both the dipole-allowed $\Gamma_5$ exciton state and the weakly allowed $\Gamma_1/\Gamma_2$ exciton states. The in-plane field $B_{\parallel c}$, which is perpendicular to the c axis, increases the oscillator strength of the weak $\Gamma_1/\Gamma_2$ states by forming a mixed exciton state.

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Zinc oxide is a direct wide-gap semiconductor of strong interest for optoelectronic applications due to its large (60 meV) exciton binding energy. Its properties have been studied for many years, with a sharp increase in activity during the past decade [1]. Despite its long history, some fundamental properties of ZnO are still not fully understood. The valence-band symmetry ordering is especially controversial. In most wurtzite semiconductors, the quasidegenerate $p$-like valence states at $\Gamma$ are split by the crystal-field and spin-orbit interactions into states of symmetry $\Gamma_9$, $\Gamma_7$, and $\Gamma_5$, in order of decreasing energy. However, Thomas and Hopfield [4], on the basis of reflectivity studies of fundamental excitonic transitions, proposed that ZnO has a negative spin-orbit splitting, leading to a reversed $\Gamma_7$–$\Gamma_9$–$\Gamma_5$ ordering.

This reversed ordering is consistent with a wide variety of experimental data (see Refs. [3, 4, 7, 8, 9] for a few examples), and is also supported by first-principles calculations [10]. Nevertheless, some authors have rejected this interpretation in favor of the conventional $\Gamma_9$–$\Gamma_7$–$\Gamma_5$ ordering [11, 12, 13, 14, 15, 16, 17, 18]. Many of the studies supporting reversed ordering did not directly compare the two possibilities; hence, although these studies provide cumulative evidence in favor of reversed ordering, they cannot be said to definitively resolve the controversy. Some such studies also used models with a large number of fitting parameters, leaving open the possibility that other parameter sets (perhaps consistent with a different ordering) might yield an equally good fit.

A more direct approach was taken in Refs. [19] and [20], which used first-principles calculations [10] and magneto-optical studies of bound excitons (BX) [20] to argue that the sign of the hole $g$ factor deduced from magneto-optical studies of free excitons (FX) in Ref. [12] is incorrect, and that the top valence band of ZnO should therefore have $\Gamma_7$ symmetry. However, as pointed out by Thomas and Hopfield [21], the hole $g$ factors derived from studies of BX may, in principle, be entirely different from the $g$ factors of free holes, due to mixing of the quasidegenerate valence states by the defect potential. For this reason, it is not a priori obvious that results based on BX are capable of providing unambiguous evidence for the symmetry of the top valence band of ZnO.

In view of the simple and well defined nature of FX, we have employed high-resolution magneto-photoluminescence (PL) of $A$ excitons to show the valence-band ordering in a more specific and straightforward way. A powerful technique, magneto-PL explicitly reveals the relationship between the fundamental optical transitions of semiconductors and the optical selection rules that are uniquely determined by the band structure symmetries. In this paper, unambiguous evidence obtained by careful and detailed magneto-PL measurements is presented to indicate, without any doubt, that the top valence band of wurtzite ZnO has $\Gamma_7$ symmetry. This interpretation is also supported by the polarization dependence of the Zeeman splitting of neutral-impurity BX.

Free excitons involving the $s$-like $\Gamma_7$ conduction band and the three valence bands are labeled as $A$, $B$, and $C$ excitons, in order of increasing exciton energy [3]. Depending on the symmetry assigned to the top valence band, the $A$ excitons have two possible symmetries:

\[ \Gamma_7 \otimes \Gamma_7 \rightarrow \Gamma_5 \oplus \Gamma_1 \oplus \Gamma_2, \quad \Gamma_7 \otimes \Gamma_9 \rightarrow \Gamma_5 \oplus \Gamma_6. \]  

Here the doubly degenerate $\Gamma_5$ exciton is dipole-allowed for light polarized normal to the hexagonal $c$ axis ($E \perp c$) and the singly degenerate $\Gamma_1$ exciton is dipole-allowed for $E \parallel c$, whereas the doubly degenerate $\Gamma_6$ exciton and the singly degenerate $\Gamma_2$ exciton are dipole-forbidden.

Using a magneto-cryostat with magnetic field $B$ up to 7 T, the magneto-PL measurements were performed on a 3 μm thick high quality ZnO thin film deposited on (0001) sapphire substrate using metal-organic chemical vapor deposition (MOCVD). The inset of Fig. 1(a) depicts the magneto-PL experimental setup. The Faraday configuration ($k \parallel B$) is applied, where $k$ is the wave vector of the emitted light and $\theta$ is the angle between $B$ and...
the $c$ axis. $B$ can be decomposed into an out-of-plane component $B_{\|} = B \cos \theta$ (parallel to the $c$ axis) and an in-plane component $B_{\perp} = B \sin \theta$ (perpendicular to the $c$ axis). In our setup, different angles $\theta$ were achieved by simply rotating the $c$ axis. The incident laser was perpendicular to the magnetic field for arbitrary $\theta$, except that the backscattering geometry was used for $\theta = 0$. The magneto-PL spectra were resolved by a monochromator (SPEX 1403) with 1800 g/mm double gratings and detected by a photomultiplier tube (R928). The spectral resolution of the system is about 0.1 meV. The circular polarization ($\sigma_+\text{ or } \sigma_-$) of the emitted light was analyzed using a quarter-wave plate and a linear polarizer. All the measurements were performed at 5 K to minimize energy shifts induced by thermal fluctuation.

To demonstrate clearly the magnetic field effect, the angular-dependent zero-field PL as well as magneto-PL spectra of the A-exciton 1S state ($FX_{A}^{n=1}$) are shown for comparison in Figs. 1(a) and 1(b), respectively. At $B = 0$ T, two resolved fine structures of $FX_{A}^{n=1}$ are labeled as $P_1$ (3.3757 eV, weak) and $P_2$ (3.3778 eV, strong), which correspond to the weakly allowed (or dipole-forbidden) and dipole-active excitons, respectively [see Fig. 1(a)]. The changes of the peak positions and intensities are found to be negligible at different $\theta$, which indicates a weak dependence on the polarization direction of the incident laser. Applying a magnetic field of 7 T, rich features are found with strong angular dependence in the PL spectra [see Fig. 1(b)]. When $\theta = 10^\circ$, Zeeman splitting of $P_1$ is observed with a splitting energy $\Delta E_{P_1}$ as large as 1.4 meV, whereas $P_2$ remains nearly unchanged. When $\theta$ increases, $\Delta E_{P_1}$ becomes smaller. The two split peaks of $P_1$ finally merge into one at $\theta = 80^\circ$. On the other hand, the integrated intensity $I_{P_1}$ of $P_1$ increases with increasing $\theta$ and eventually dominates the $FX_{A}^{n=1}$ spectrum. It is worth noting that there is almost no change in the magneto-PL spectrum at $\theta = 0^\circ$ when $B$ is scanned from 0 T to 7 T, which is due to the weakly allowed (or dipole-forbidden) nature of $P_1$ at $B_{\perp c} = 0$. The in-plane magnetic field $B_{\perp c}$ is found to significantly increase the oscillator strength of $P_1$, which will be explained below.

We interpret the experimental data using a simple quasi-cubic model [3] in which the crystal-field splitting $\Delta_{cr}$ and the spin-orbit splitting $\Delta_{so}$ are assumed to satisfy $|\Delta_{so}| < |\Delta_{cr}|$. We treat $\Delta_{so}$ as a perturbation of $\Delta_{cr}$, working to first order in the energy and to zeroth order in the state vector. If we choose the $z$ and $c$ axes to be the same, the exciton states formed from the $p_x \pm ip_y$ hole states of $\Gamma_7$ symmetry (i.e., the $A$ excitons according to Thomas and Hopfield) are therefore

$$|\Gamma_5^{(7)}(\pm) = |s\pm\rangle|\pm\rangle, (g_{exc} = g_h^\parallel + g_e), \quad (2a)$$

$$|\Gamma_1^{(7)}{\pm} = |s\mp\rangle|\pm\rangle, (g_{exc} = g_h^\parallel - g_e). \quad (2b)$$

Here $|s+\rangle|m, -\rangle$ is the tensor product of a spin-up $s$ electron and a spin-down $p$ hole whose $z$ component of orbital angular momentum is $m$. The $\pm$ label of the exciton states is taken from the sign of $m$ (note that for $\Gamma_5$, $m$ is also the $z$ component of the total exciton angular momentum). In Eq. (2b), the contribution of $\Delta_{so}$ to the short-range exchange interaction is neglected, so that $\Gamma_1$ and $\Gamma_2$ form an approximately doubly-degenerate reducible representation denoted $\Gamma_1{\pm}2$. A small field $B_{\| c}$ produces a linear Zeeman splitting with the given exciton effective $g$ factors $g_{exc}$, in which $g_e$ is the (nearly) isotropic electron $g$ factor and $g_h^\parallel$ is the hole $g$ factor parallel to the $c$ axis. In the simple model of Ref. [19] we have $g_h^\parallel = 2K - g_0$, where $K = -(3\kappa + 1)$ is the magnetic Luttinger parameter and $g_0 = 2$ is the $g$ factor of a free hole. The states in Eq. (2a) are dipole-forbidden when $B_{\perp c} = 0$, but they become dipole-allowed when $B_{\perp c} \neq 0$ due to mixing with $|\Gamma_5^{(7)}(\pm)$ or $g_{exc}$.

Likewise, the exciton states formed from the $p_x \pm ip_y$ hole states of $\Gamma_9$ symmetry (i.e., the $B$ excitons according to Thomas and Hopfield) are given by

$$|\Gamma_5^{(9)}(\pm) = |s\mp\rangle|\pm\rangle, (g_{exc} = g_h^\parallel - g_e), \quad (3a)$$

$$|\Gamma_6(\pm) = |s\pm\rangle|\pm\rangle, (g_{exc} = g_h^\parallel + g_e). \quad (3b)$$

in which $g_{h}^\parallel = 2K + g_0$. Just as for $|\Gamma_1{\pm}2, \pm\rangle$, the states $|\Gamma_6, \pm\rangle$ are dipole-forbidden when $B_{\perp c} = 0$, but become dipole-allowed when $B_{\perp c} \neq 0$ due to $g_{exc}$-induced mixing with $|\Gamma_5^{(9)}(\pm)$.

The above model is crude, but it has the advantage of explaining the main features of the experiment in a simple way. We have also considered a more complicated 12-dimensional 1S-exciton Hamiltonian [19] that includes a full treatment of spin-orbit coupling and the short- and long-range exchange interactions, but the results were
FIG. 2: (Color online) Schematic representations of energy levels of A-exciton transitions involving holes of (a) $\Gamma_5$ symmetry and (b) $\Gamma_6$ symmetry. (c) shows the circular polarization dependence of the magneto-PL of FX$_n^+$.

The experimentally determined zero-field exchange splitting $\delta$ is 2.1 meV, which is in good agreement with Refs. [1], [3], and [22].

To get more information on the electron and hole $g$ factors, the magnetic field dependences of the transition energies of $P_1$ and $P_2$ are summarized in Figs. 3(a) and 3(c) for $\theta = 20^\circ$ and $\theta = 80^\circ$, respectively. Figure 3(b) shows the $\theta$ dependence of $P_1$ and $P_2$ at $B = 7$ T. In the Zeeman splitting of $P_1$ and $P_2$, $B_{\perp}$ lifts the degeneracy of the $P_1$ ($\Gamma_{12}$) states or the doublet $P_2$ ($\Gamma_5$) state. The energy splitting of $P_1$ ($\Gamma_{12}$) is fitted using $E_{P_1\pm} = E_{P_1} \pm \frac{1}{2}(g_h - g_e)\mu_B B_{\parallel}$, where $\mu_B$ is the Bohr magneton and $E_{P_1} = 3.37576$ eV is the zero-field transition energy of $P_1$ ($\Gamma_{12}$). Using $g_e = 1.95$ [22], the hole $g$ factor obtained from the fitting (see solid curves in Fig. 3) is $g_h = -1.6$, which agrees well with the values obtained in Refs. [3] and [6] (but with a different convention for the sign of $g_h$). The fact that the Zeeman splitting for $P_2$ ($\Gamma_5$) could not be resolved (see black dots in Fig. 3) indicates the nearly equal absolute values of $g_e$ and $g_h$. The dotted curves for $P_2$ are plotted according to $E_{P_2\pm} = E_{P_2} \pm \frac{1}{2}(g_h - g_e)\mu_B B_{\parallel}$, employing $g_e = 1.95$ and $g_h = -1.6$.

In addition, the Zeeman splitting of BXs $I_5$ and $I_6$ [24] has also been observed, and the transition energies are shown in Fig. 3. The circular polarization depen-
dences indicate that $I_5$ and $I_6$ are excitons bound to neutral impurity centers with $A$ holes involved [20]. The dashed lines are fitted results given by $\pm \frac{\mu_B}{2} B (g_e + g_h)$ and $g_h = g_\| \sqrt{\cos^2 \theta + (g_\perp^2 / g_\|^2) \sin^2 \theta}$, where $g_e = 1.95$, $g_\| = -1.6$, and $g_\perp = 0.11$. The equality of the fitted FX and BX values of $g_e$ provides ex post facto support for the conclusions of Ref. [20] (although, as noted in the introduction, such similarity cannot be assumed to hold in general).

The different contributions of the in-plane and out-of-plane magnetic field to the magneto-PL spectra are shown more specifically in Fig. 4. The left panel [Fig. 4(a)] shows the measured $B_{||c}$ dependence of the Zeeman splitting $\Delta E_{P_1}$ of $P_1 (\Gamma_{1\parallel 2})$ (solid dots). The dashed line is a guide for the eyes.

FIG. 4: (Color online) (a) $B_{||c}$ dependence of the Zeeman splitting $\Delta E_{P_1}$ of $P_1 (\Gamma_{1\parallel 2})$. (b) $B_{\perp c}$ dependence of the intensity $I_{P_1}$ of $P_1 (\Gamma_{1\parallel 2})$ (solid dots). The dashed line is a guide for the eyes.

wurtzite ZnO was found to have $\Gamma_7$ symmetry with no ambiguity by directly examining the polarization of the $A$-exciton emission. The out-of-plane component $B_{\perp c}$ of the magnetic field was found to be responsible for the linear Zeeman splitting of the $\Gamma_5$ and $\Gamma_1/\Gamma_2$ states. The in-plane magnetic field $B_{||c}$ increases the intensity of the originally weakly allowed $\Gamma_1/\Gamma_2$ states by mixing with $\Gamma_5$ states. The hole effective $g$ factor was found to be negative and has the value $-1.6$.

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