Valence band ordering and magneto-optical properties of bound excitons in ZnO

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Bulk ZnO is a direct band gap semiconductor where the valence band maximum is split in a triplet by the wurtzite crystal-field and spin-orbit interaction. The symmetry of the upper valence subband has been the subject of controversy (Γ_7 or Γ_9 character) for more than 40 years. Most of the magneto-optical investigations of free and bound excitons in ZnO are incomplete and allow both interpretations concerning the symmetry of the holes involved. In this paper we present the results of the detailed theoretical and experimental studies of the magneto-optical properties of the bound excitons in bulk ZnO and confirm the Γ_7 symmetry of the upper valence subband.

We analyze theoretically the Zeeman splitting of the excitons bound to the ionized centers and excitons bound to neutral donor or acceptor centers for both Γ_7 and Γ_9 symmetries of the valence band. Our calculations show that the Zeeman splitting of the Γ_7 (Γ_9) holes in magnetic field parallel to the hexagonal c axes of the crystal is smaller (larger) than the Zeeman splitting of the electrons. We find that the magneto-luminescence measurements performed in Faraday geometry with right and left circular polarized light can be well described for Γ_7 as well as for Γ_9 symmetry. However, the fitting of experimental dependence of Zeeman splitting on the angle between magnetic field and c axis shows that holes involved in all low temperature bound exciton transitions and thus the upper valence subband have the Γ_7 symmetry. The hole g-factors determined for excitons bound to an ionized and neutral impurity center are close to each other and to the g-factor calculated for the Γ_7 hole in free exciton ground state. This allows us to suggest a donor character of the neutral impurity centers. This conclusion is confirmed by the temperature-dependent magneto-transmission and magneto-luminescence measurements.