Co dopant in ZnO: ionization *vs* internal optical transitions

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Experimental studies of Co:ZnO show that Co substitutes for Zn, and acquires the Co^{2+} (d^7) electronic configuration with spin 3/2. Two characteristic optical transitions involving Co are observed, namely the internal transition $e_{2\downarrow} \rightarrow t_{2\downarrow}$ ($^4A_2 \rightarrow {}^4T_1$) at about 2.0 eV seen in both absorption and emission, and the ionization transition beginning at 2.6 eV transferring a d(Co) electron to the conduction band.

Previous calculations suggested that Co induces the $e_{2\downarrow}$ level in the forbidden band gap, which are fully occupied by electrons, while the empty $t_{2\downarrow}$ state is resonant with the continuum of the conduction band, see Fig. 1 (a) and (d). In this situation, the ionization energy is expected to be lower than the internal $e_{2\downarrow} \rightarrow t_{2\downarrow}$ transition, in contrast to the experimental data.

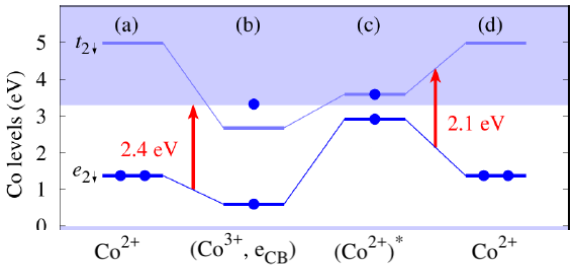

Fig. 1. Single particle Co levels in ZnO for (a) and (d) ground state configuration of Co^{2+}, (b) Co^{3+} and (c) excited state of Co^{2+} , after $e_{2\downarrow} \rightarrow t_{2\downarrow}$. U(Co) = 3 eV.

To explain this result, the electronic structure of Co:ZnO is investigated by density functional theory in the generalized gradient approximation. By applying +U corrections to d(Zn), d(Co) and p(O) orbitals we reproduce the band structure of pure ZnO and Co:ZnO.

As a result of strong electron-electron intrashell repulsion and the non-vanishing +U corrections, one-electron energies strongly depend on the occupations of levels, as showed Fig. 1. Consequently, the transition energies cannot be calculated from the differences of energy levels of Co^{2+}. In particular, ionization of Co^{2+} induces a strong, ~2 eV, downward shift of Co levels due to the reduced Coulomb intrashell repulsion, Fig. 1b. Internal $e_{2\downarrow} \rightarrow t_{2\downarrow}$ transition changes the occupation of Co levels thus changing energy levels caused by the occupation-dependent +U(Co) corrections, Fig. 1c. Interestingly, after the internal transition, the excited electron is about 0.25 eV above conduction band minimum (CBM). However, it cannot spontaneously ionize to the CBM, because the ionized configuration (Co^{3+}) has the empty $t_{2\downarrow}$ level below CBM, and the total energy of Co^{3+} state is higher than that of $(Co^{2+})^*$. Consequently, the internal transition does not result in photoconductivity, in agreement with experiment.

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