# Metastability of $Mn^{3+}/Mn^{2+}$ in ZnO: theory and experiment

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Current interest in ZnO:Mn crystals is motivated by their application to water-splitting by sun-light for clean hydrogen production, which is an important subject of ongoing research. Doping with Mn introduces an $Mn^{3+}$/ $Mn^{2+}$ mid-gap energy level, which shifts the absorption to lower energies, making it more compatible with the sun spectrum.

ZnO crystals containing 0.1–2 % of Mn were grown by the Chemical Vapor Transport (CVT) method. The crystals exhibit strong optical absorption in the energy region below the band gap, which partially overlaps with the fundamental absorption, as well as very strong EPR signals characteristic for isolated $Mn^{2+}$ ions. The absorption has been associated with the charge-transfer transition ($Mn^{2+} \rightarrow Mn^{3+} + e_{CB}$) [1]. At low temperatures, the EPR signal is efficiently quenched by the illumination in the spectral region of the $Mn^{2+}$ absorption. With increasing illumination power the $Mn^{2+}$ EPR lineshape changes from Gaussian to Dysonian, which is a proof of the increased conductivity of the samples. Moreover, the interaction of localized spins with the carrier spins leads to a change of the $Mn^{2+}$ g-factor. The only model reproducing both the temperature and illumination power dependencies of the $Mn^{2+}$ EPR signal photo-quenching requires that there is an additional, other than $Mn^{2+}$, source (e.g. native defects) of photoinduced carriers.

Electronic structure of Mn in ZnO was calculated using the GGA+U method [2, 3]. The calculated ionization energy of ($Mn^{2+} \rightarrow Mn^{3+} + e_{CB}$) is 2.0 eV, in good agreement with experiment. After ionization, $Mn^{3+}$ is metastable because of both large atomic relaxations of the Mn neighbors, and the very high intracenter Coulomb repulsion of *d*(Mn) electrons. Recombination requires overcoming an energy barrier estimated to ~20 meV, in agreement with the observed photoquenching of $Mn^{3+}$ at low temperatures.

[1] J. Gilliland et al., App. Phys. Lett. **96**, 241902 (2010)
[2] M. Cococcioni, S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).
[3] Quantum Espresso package, see www.pwscf.org.

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