Electronic and magnetic structure of *3d* impurities in ZnO: Fermi level effects on *p-d* coupling

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Functionalization of ZnO aimed at various applications, such as photovoltaics, promotes studies of ZnO doping with various transition metal (TM) impurities. Both experimental and theoretical effort is currently directed towards this goal.

We performed a systematic study of impurity levels of TMs impurities ranging from Ti to Ni. Density functional theory was employed, together with the +U correction in order to improve both the ZnO host band structure (including the band gap) and the TM levels. The choice of the U(TM) values is based on the experimental data where available. The calculations use large supercells method, and include full structural relaxations.

TM-induced levels are studied as a function of the Fermi level position. In several cases, such as Ti, V, and Cr, the impurities can have a resonance donor character, leading to the n-type conductivity, and which possibly mediates a long-range ion-ion magnetic coupling. In other cases, the energies of the gap states were determined. The impact of the energy distance between TM level and the valence band maximum on the exchange coupling of TM with free holes is demonstrated. In particular, the coupling constant can substantially depend on the TM charge state, which is the case of Mn or Fe.

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