Transition metal ions in ZnO: theory of the $s, p-d$ exchange coupling

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The $s, p-d$ exchange coupling between free carriers and $d-$electrons of the transition metal (TM) dopants constitutes the basic feature of diluted magnetic semiconductors. We study the TM dopants ranging from Ti to Cu in ZnO within the density functional theory [1]. The $+U$ terms are employed to improve both the ZnO band structure and the position the TM levels. Detailed features of each ion are analysed, and general trends are indicated.

The $s-d$ coupling constant $N_0\alpha$ is almost the same for all TM ions, 0.5 eV. In contrast, the $p-d$ constant $N_0\beta$ varies about 10 times when going from V to Cu. In the cases of Fe, Co and Ni, the sign of $N_0\beta$ depends on the charge state of dopant, since the constant is positive (i.e. ferromagnetic) for 2+ and negative (antiferromagnetic) for 3+ ions. Moreover, $N_0\beta$ for light holes and heavy holes can differ by a factor 2, or even have opposite signs. These unexpected features of $N_0\beta$ were not recognized in previous investigations.

Analysis of the wave functions of ZnO:TM reveals the leading mechanisms of both $s-d$ and $p-d$ couplings. Those mechanisms are different for electrons and holes because of the different symmetries of their wave functions. In agreement with the Anderson picture, the main features of the $N_0\beta$ constant are determined by the $p-d$ hybridization between the d(TM) and p(O) orbitals, and thus by the energies of TM levels relative to the valence band maximum. In turn, the $N_0\alpha$ originates mainly in the intra-atomic direct exchange between the s and d electrons of the dopant ion. However, the spin polarization of the oxygen neighbours of the TM ion induced by the $p-d$ hybridization leads to the spin polarization of the s(O) orbitals, which enhances the value of $N_0\alpha$. A reasonable agreement with experimental data is obtained.

References:

[1] A. Ciechan and P. Bogusławski, Scientific Reports **11**, 3848 (2021).

The authors acknowledge the support from the Projects No. 2016/21/D/ST3/03385, which are financed by Polish National Science Centre (NCN). Calculations were performed on ICM supercomputers of University of Warsaw (Grant No. GB84-37 and G16-11).