s, p - d coupling in ZnO doped with 3d transition metal impurities

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Motivations

- The $s,p-d$ coupling between free carriers and the localized $d-$electrons of the TM dopants constitutes the basic feature of diluted magnetic semiconductors. The magnetic properties of ZnO:TM are explored because of possible application in spintronics or solotronics [1].
- We study electronic and magnetic properties of ZnO:TM and determine dominant mechanisms of coupling with localized spins of magnetic atoms for both electrons and holes [2].

DFT methods

The calculations are performed within the DFT witin the GGA+U approximation [3]. We use the pseudopotential method implemented in the Quantum ESPRESSO code [4]. Analysis of a single TM impurity in ZnO is performed using $3\times3\times2$ supercells with 72 atoms.

U corrections for 3d(TM), 3d(Zn) and 2p(O) electrons:

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	O
U (eV)	2.0	2.0	2.0	1.5	4.0	3.0	3.0	2.0	12.5	6.25

The values of U corrections give a correct band structure of ZnO and lead to an excelent agreement with experimental optical properties of TM ions in ZnO [5].

TM levels in ZnO

Effect of intrashell Coulomb repulsion [6]:
TM levels increase with increasing occupation

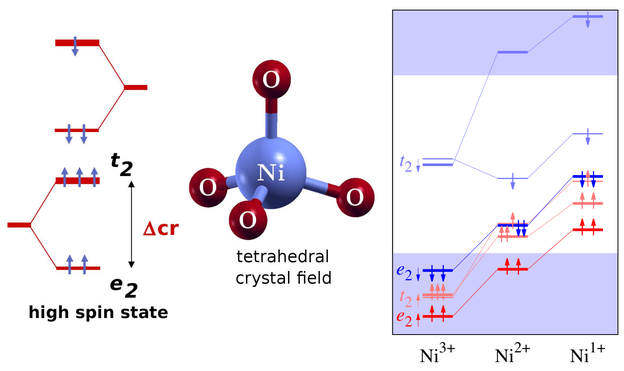

Figure 1: *(left) Spin splitting and CF splitting of TM level in ZnO. (right) The energy levels of TM in various charge state.*

TM^{2+} levels
levels decrease with increasing atomic number

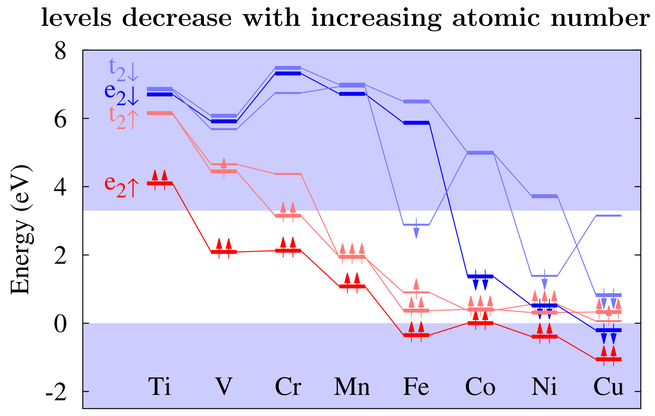

Figure 2: *Energy levels of TM^{2+} ions in ZnO.*

sp-d magnetic coupling

Exchange constants are calculated from

$$N_0\alpha = \Delta\varepsilon_c/(x\langle S\rangle), \qquad N_0\beta = \Delta\varepsilon_v/(x\langle S\rangle),$$

where $\Delta\varepsilon_c$ and $\Delta\varepsilon_v$ - spin splittings of CBM and VBM, x - concentration of the TM ions, $\langle S\rangle = M/2$ - total magnetic moment.

$N_0\alpha$ and $N_0\beta$

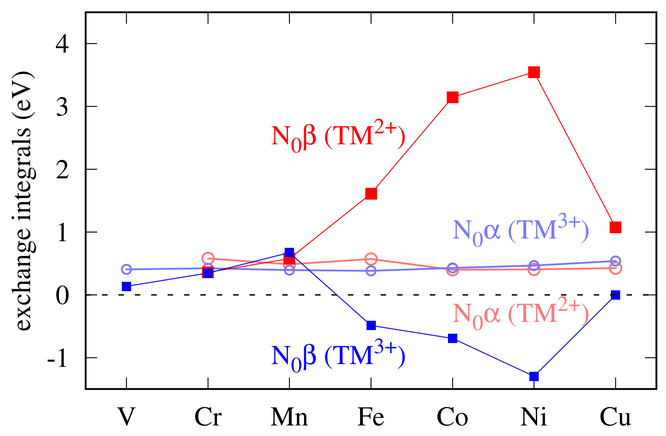

Figure 3: *The exchange integrals $N_0\alpha$ and $N_0\beta$ for ZnO with TM in 2+ and 3+ charge state.*

Spin density and xc perturbation

In spin polarized system $\Delta n = n_\uparrow - n_\downarrow \neq 0$ and thus

$$\Delta V_{xc} = V_{xc\downarrow} - V_{xc\uparrow} \approx A(n_\downarrow^{1/3} - n_\uparrow^{1/3})$$
$$\Delta\varepsilon_c = \langle CBM\downarrow|V_{xc\downarrow}|CBM\downarrow\rangle - \langle CBM\uparrow|V_{xc\uparrow}|CBM\uparrow\rangle$$

if $|CBM\uparrow\rangle = |CBM\downarrow\rangle$ then simply:

$$\Delta\varepsilon_c = \langle CBM|\Delta V_{xc}|CBM\rangle$$

Both Δn and ΔV_{xc} dominated by d(Co) with contribution of p(O-nn)

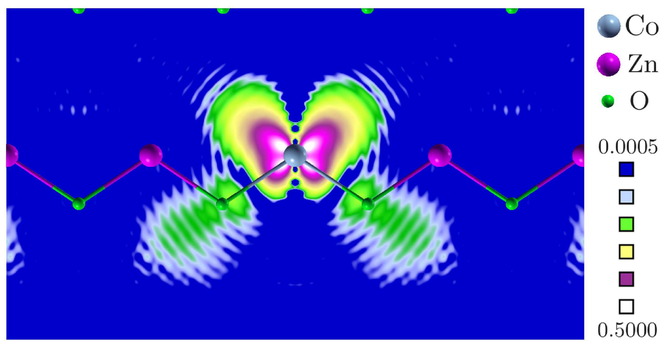

Figure 4: *Two-dimensional plot of $n_\uparrow^{1/3} - n_\downarrow^{1/3}$ of ZnO with Co 2+ in the plane containing Co-O bonds.*

$N_0\alpha$ constant and s-d coupling

CBM: s(O)+s(Zn)+s(TM) states

- on-site direct exchange on TM ion (70%, Liu picture) and
- on O-nn caused by p(O)-d(TM) hybridization (30%, new effect)
- $s-d$ coupling is always FM, $N_0\alpha$ silimar for all ions

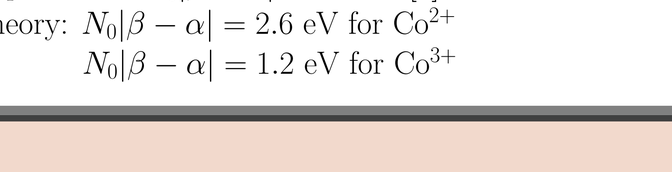

Figure 5: *The wave functions squared of the CBM of ZnO:Co^{2+}.*

$N_0\beta$ constant and p-d coupling

VBM: p(O)+p(Zn)+d(TM)

- kinetic exchange caused by strong p(O)-d(TM) hybridization
- $sp-d$ can be FM ($N_0\beta>0$) or AFM ($N_0\beta<0$)

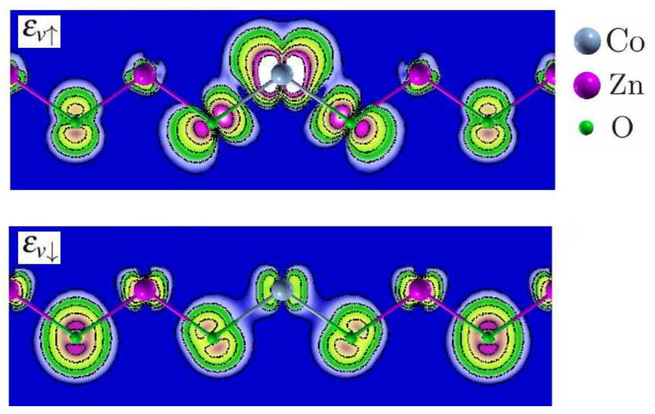

Figure 6: *The wave functions squared of the VBM of ZnO:Co^{2+}.*

Sign of $N_0\beta$ - Anderson model

$$N_0\beta \sim \Delta\varepsilon_v = \frac{1}{2}\left(\frac{|V_{hop}|^2}{\varepsilon(t_{2\uparrow}) - \varepsilon_v} - \frac{|V_{hop}|^2}{\varepsilon(t_{2\downarrow}) - \varepsilon_v}\right)$$

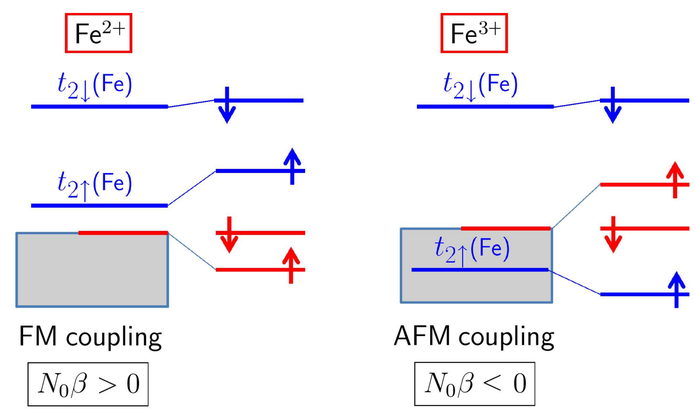

Figure 7: *Dependence of the sign of $N_0\beta$ exchange constant on the position of $t_{2\sigma}$ levels of TM ion.*

⇓

Change of sign of $N_0\beta$
dependence of $p-d$ coupling on the charge state caused by intra-shell Coulomb repulsion:
$N_0\beta<0$ for Fe^{3+}, Co^{3+}, Ni^{3+}, Cu^{3+}

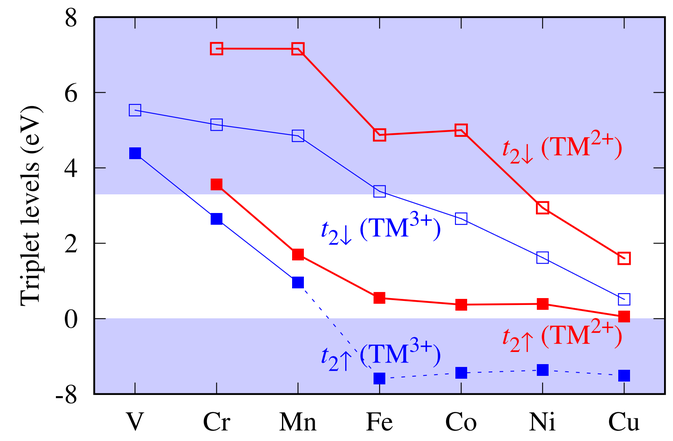

Figure 8: *The triplet levels of TM^{2+} and TM^{3+} ions in ZnO.*

Comparison with experiment

Ti, V, Cr
experiment: $N_0\alpha = N_0\beta \approx 0$ [7]
theory: Ti - non-magnetic; V, Cr - very weak coupling

Mn - good agreement
experiment: $N_0|\beta-\alpha| = (0.2\pm0.1)$ eV [8]
theory: $N_0|\beta-\alpha| = 0.1$ eV for Mn^{2+}

Co - close to experiment
experiment: $N_0|\beta-\alpha| = 0.8$ eV [9]
theory: $N_0|\beta-\alpha| = 2.6$ eV for Co^{2+}
$N_0|\beta-\alpha| = 1.2$ eV for Co^{3+}

Conclusions

- The $s-d$ coupling between magnetic moment of TM ion and conduction band electrons is always FM and the exchange constant $N_0\alpha \approx 0.5$ eV. It is caused by on-site direct exchange on TM ion as well as on nearest-neighbour O ions, which magnetic properties result from p(O)-d(TM) hybridization.
- In turn, the $p-d$ coupling with the valence band holes strongly depends on the position of TM levels in the gap. For some ions like Fe, Co, Ni, the coupling changes the sign from FM ($N_0\beta>0$) to AFM ($N_0\beta<0$) going from 2+ to 3+ charge state.

Acknowledgements

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