SIC-LSD study of transition metal valencies in oxide materials

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Transition metal doped ZnO: DMS?

Two competing theoretical approaches:

- **Zener model** Dietl *et al.* Semicond. Sci. and Technol. **17** (2002)
  - **d-d correlations >> band formation**
  - **Tm^{2+} ions provide localized spin**
  - **ferromagnetism mediated by delocalized carriers**
- **Band model** Sato *et al.*, Semicond. Sci. Technol. **17** (2002)
  - **d-d correlations << band formation**
  - **Exchange-split d-band**
  - **ferromagnetism due to double-exchange**

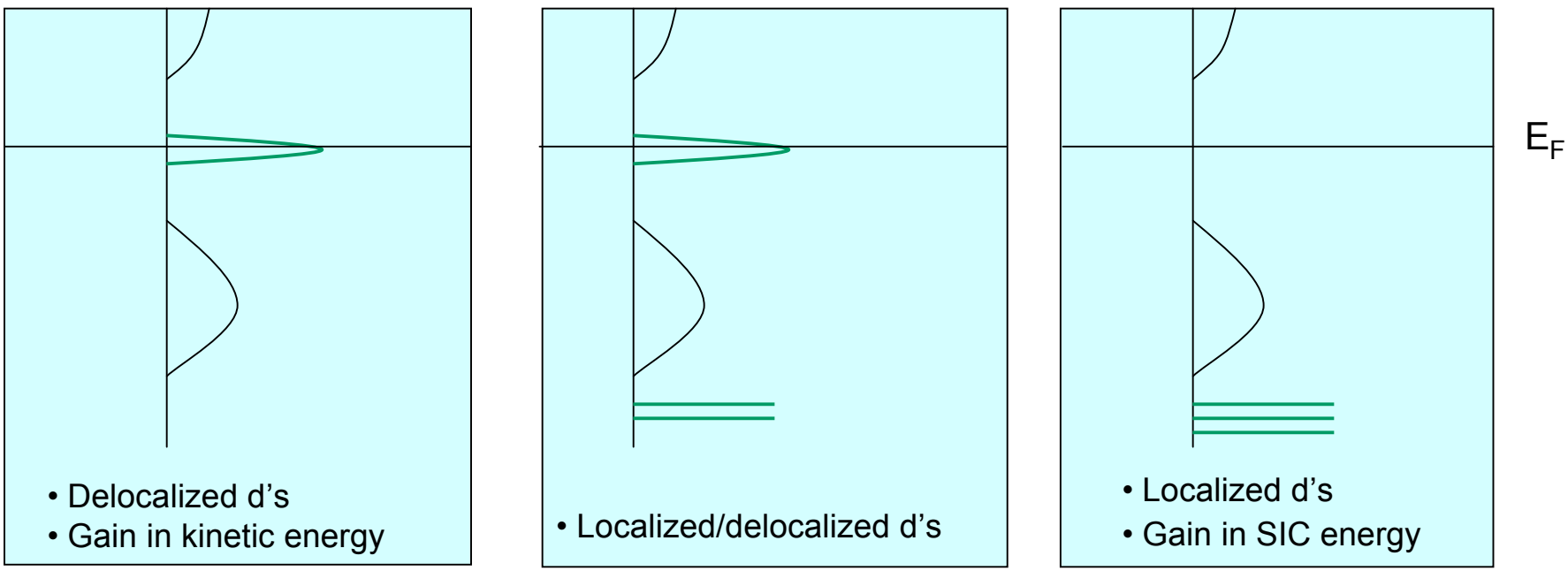
SIC-LSD method

⇒distinguish between the models based on their total energy

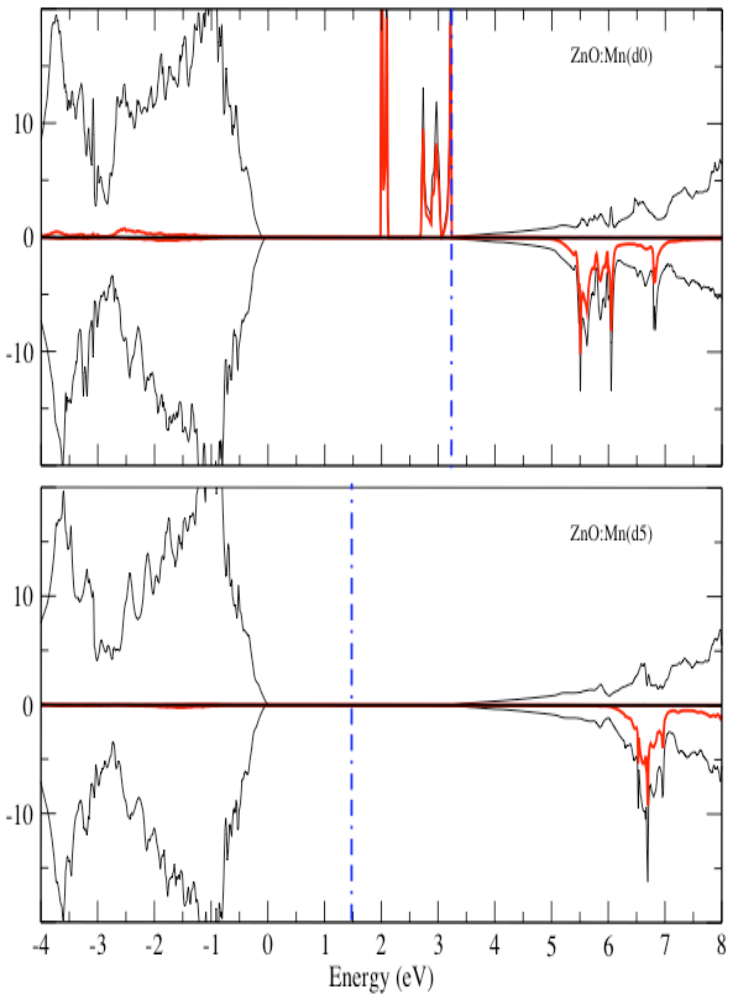
- LSD approximation to E_{XC}→ unphysical self-interaction (SI)
- SIC-LSD: energy contribution for a *d*-electron to localize:

$$E^{SIC-LSD} = E^{LSD} - \sum_{\alpha}^{occ.} \delta_{\alpha}^{SIC}$$

$$\delta_{\alpha}^{SIC} = U[n_{\alpha}] + E_{XC}^{LSD}[n_{\alpha}]$$



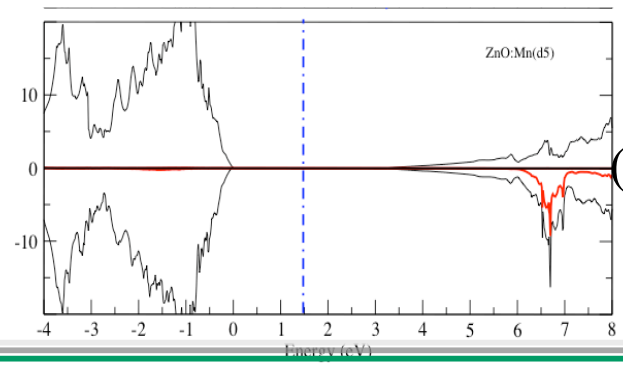
$Zn_{1-x}Mn_xO$



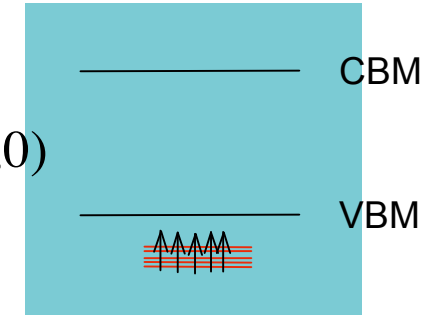
- itinerant d-states
- spin ↑ filled / spin ↓ empty
- no double exchange ⇒ no FM
- total energy: -110.120 eV

- 5 localized spin ↑ d-states
- Mn^{2+} configuration
- no hole carriers ⇒ no FM
- total energy: -113.125 eV

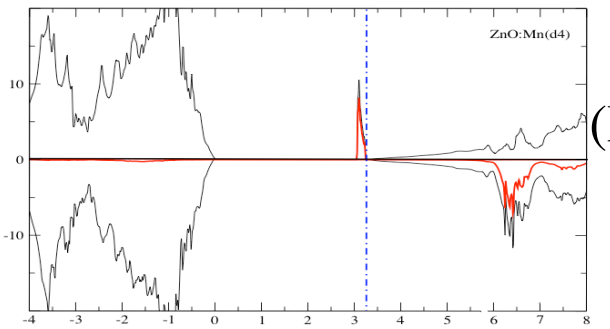
Zener model energetically more favourable than band picture



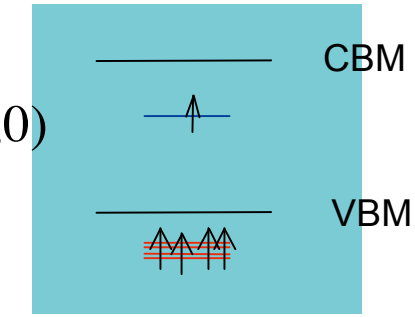
$(Mn^{2+};0)$



- Divalent neutral impurity, d^5
- E_{div}=-113.125 eV
- groundstate



$(Mn^{3+};0)$

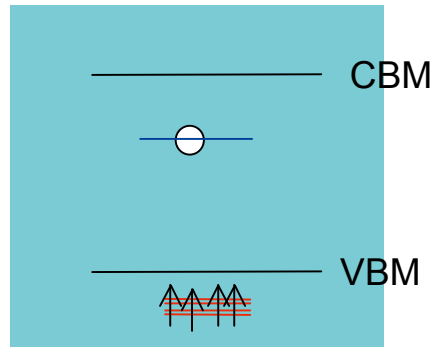


- Trivalent neutral impurity, d^4
- gap state
- E_{triv}=-112.60 eV

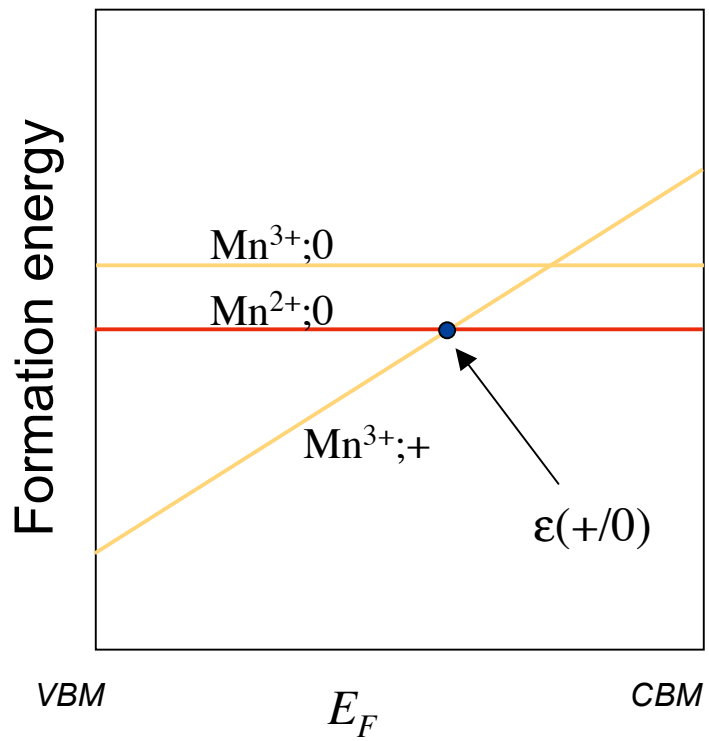
Delocalization process: $(Mn^{2+};0) \rightarrow (Mn^{3+};+) + e^-$

- **d-electron transferred to conduction band**
- **dependent on Fermi level position**
- **introduces donor level ε(0/+) in the gap**

$(Mn^{3+};+)$

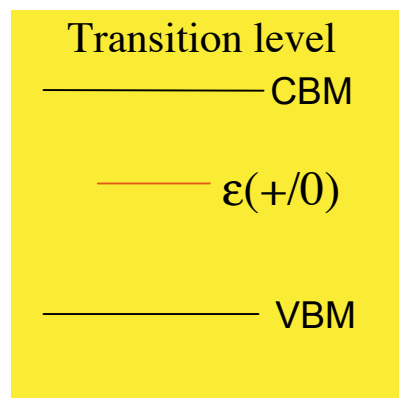


$$E_{form.}(ZnO:Mn^{v};q)=E_{tot}(ZnO:Mn^{v};q)-E_{tot}(ZnO)-\mu_{Zn}+\mu_{Mn}+q\bullet E_F$$



Donor level is defined by the Fermi energy where
$E_{form}(ZnO:Mn^{2+};0)=E_{form}(ZnO:Mn^{3+};+)$

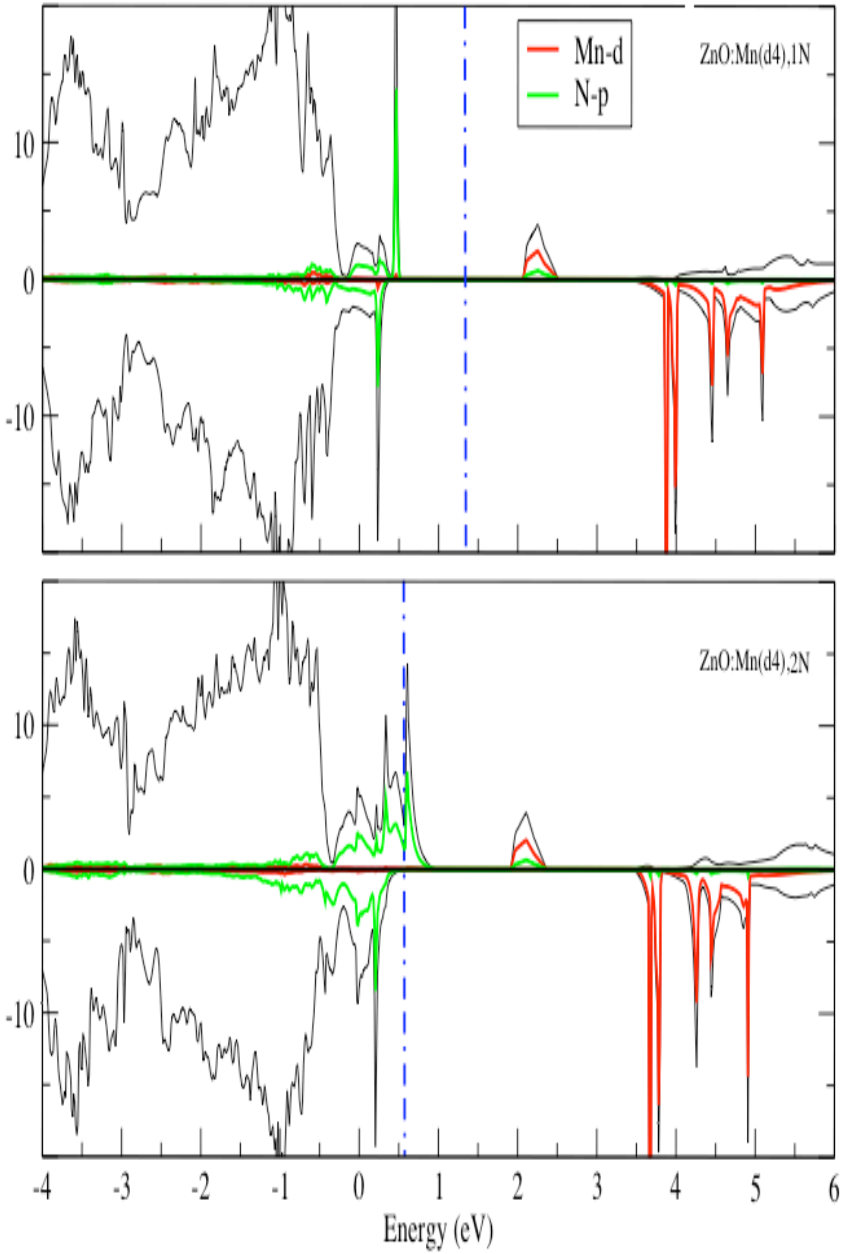
- For n-type conditions (E_F close to CBM) Mn is in neutral charge state and has valence 2+.
- For p-type conditions (E_F close to VBM) Mn is in donor charge state and has valence 3+.



•The transition level ε(+/0) is predicted to occur at near the middle of the gap as found experimentally.

ZnMnO:N

Petit *et al.*, cond-mat/0410628



- $Zn_{15/16}Mn_{1/16}O_{15/16}N_{1/16}$
- $E(Mn^{3+}) < E(Mn^{2+})$
- four SIC-localized d-levels; one delocalized d-state in the gap
- N doping ⇒ acceptor level
- Charge transfer ⇒ compensation
- no hole carriers ⇒ no FM

- $Zn_{15/16}Mn_{1/16}O_{14/16}N_{2/16}$
- Mn^{3+} remains groundstate
- Fermi level cuts N impurity band
- Hole mediated FM is now theoretically possible
- [N]>[Mn]: considerable hurdle

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Summary and Conclusions

- $\varepsilon(0/+)$ donor level situated in the ZnO gap
- ZnOMn
  - Mn is in localized d^5 state
  - Zener model energetically more favorable than band model
  - No hole carriers $\Rightarrow$ no ferromagnetic exchange
- ZnOMn:N ; [N] ≤ [Mn]
  - Mn is in d^4 state
  - No delocalized carriers
- ZnOMn:N ; [N] > [Mn]
  - Mn is in d^4 state
  - Hole states at VBM
  - Carrier induced FM possible

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