sp-d exchange coupling in Mn doped GaN and ZnO studied by magnetospectroscopy

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Outline

- Introduction
- Samples and experimental setup
- Results
  - Zero field reflectivity and photoluminescence
  - Magnetoreflectivity spectra and their model description
  - Exchange integral determination: (Ga,Mn)N and (Zn,Mn)O
  - Photoluminescence of (Zn,Mn)O in magnetic field
- Conclusions

p-d exchange integral – chemical trends

DMSs based on :

ZnTe, CdTe

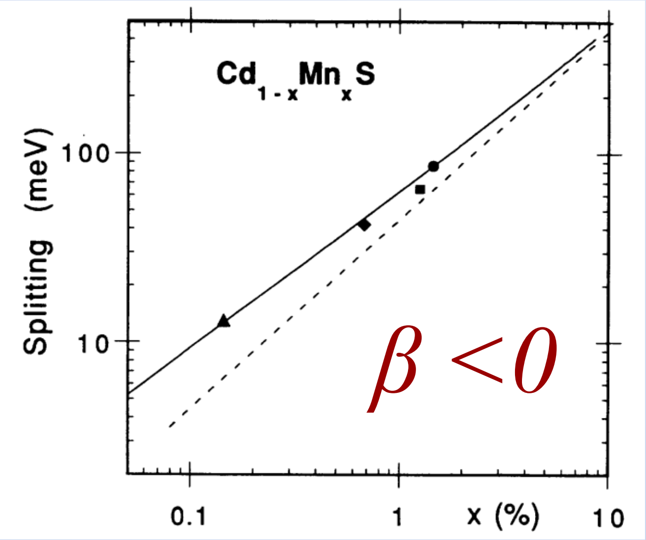
• Molecular field approximation ✓
• Virtual crystal approximation ✓

$\beta < 0$

CdS

S. Gubarev et al., JETP (1986),
M. Nawrocki et al., MRS Proc. (1987).
C. Benoit à la Guillaume et al., PRB (1992).
J. Tworzydło, PRB (1994); APPA (1995).

• Description based on virtual crystal approximation not fully correct

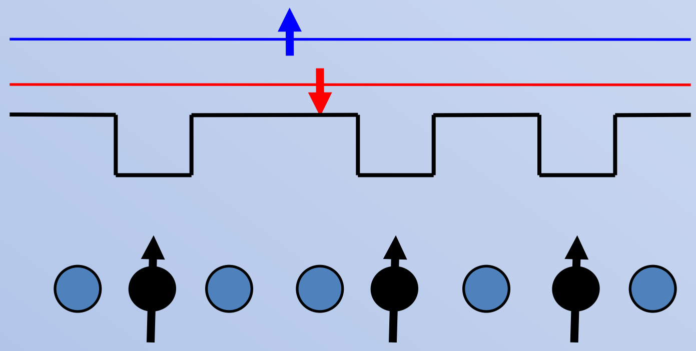


GaN, ZnO

(Zn,Co)O: W. Pacuski et al., PRB (2006).
(Ga,Mn)N: W. Pacuski et al., PRB (2007).
(Ga,Fe)N: W. Pacuski et al., PRL (2008).
(Ga,Mn)N: J. Suffczyński et al., PRB (2011).
(Zn,Mn)O: W. Pacuski et al., PRB (2011).

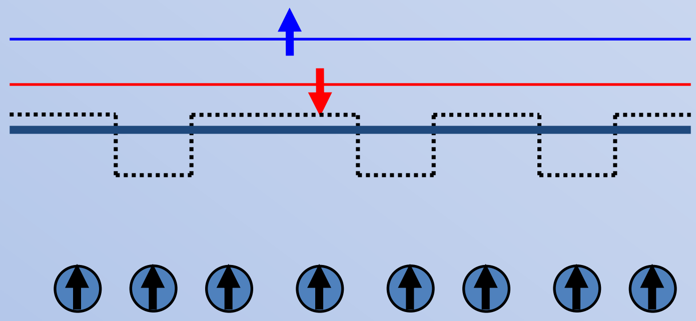
• Virtual crystal approximation fails
T. Dietl, PRB (2008).
C. Śliwa and T. Dietl, PRB (2008).

Beyond Virtual Crystal Approximation



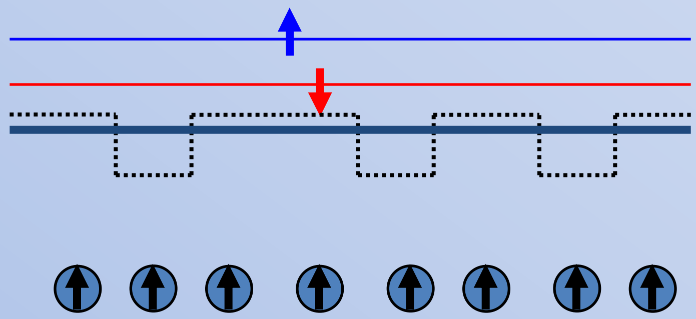
Virtual crystal
approximation
justified

Beyond Virtual Crystal Approximation



Virtual crystal approximation justified

Beyond Virtual Crystal Approximation



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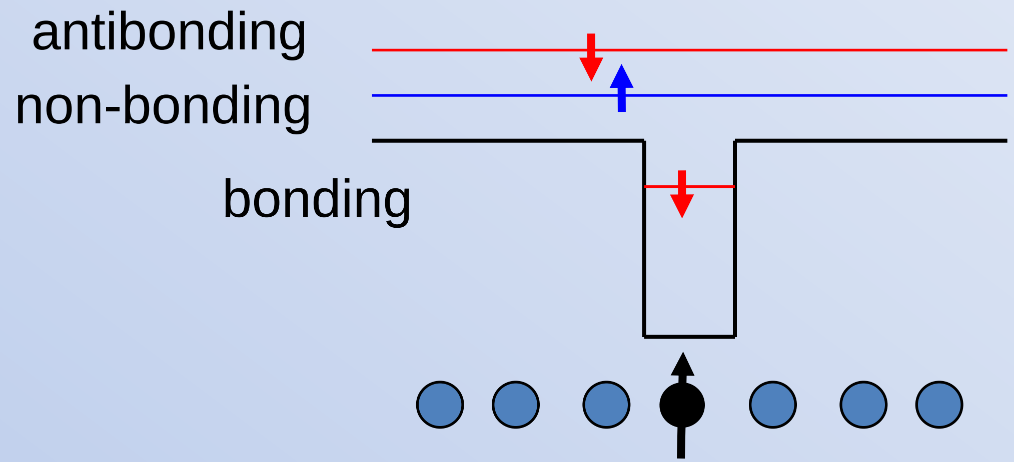

Strong coupling
- virtual crystal
approximation
does not work

(an analogue of Kondo effect in metals)

T. Dietl, Phys. Rev. B 77, 085208 (2008).
C. Śliwa and T. Dietl, Phys. Rev. B 78, 165205 (2008).
C. Benoit à la Guillaume et al., Phys. Rev. B 46, 9853 (1992).
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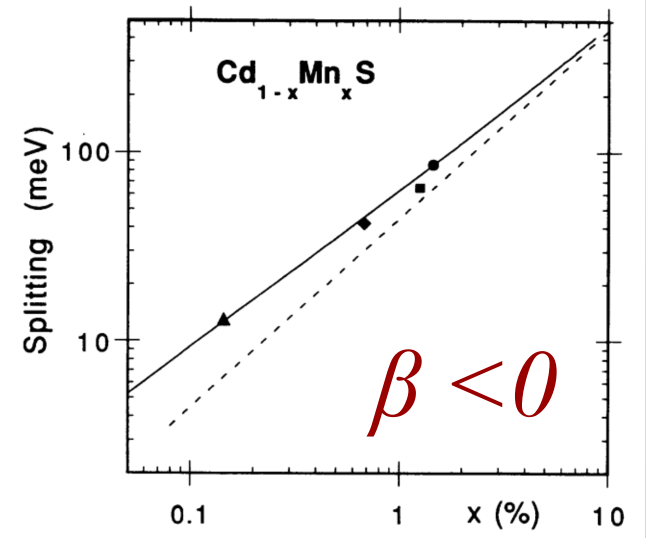

$\beta < 0$

GaN, ZnO

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(Ga,Mn)N: W. Pacuski et al., PRB (2007).
(Ga,Fe)N: W. Pacuski et al., PRL (2008).

- Virtual crystal approximation fails

$\beta^{(app)} > 0$

$\beta^{(app)}$ *reduced*

$\alpha^{(app)}$ *reduced*

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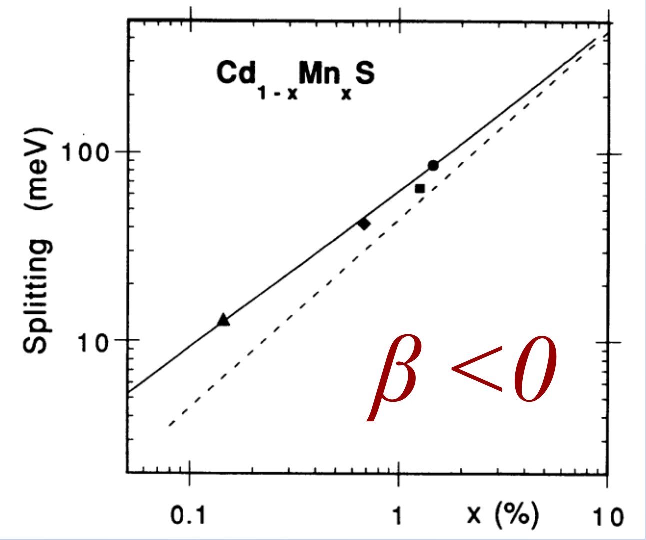

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- Virtual crystal approximation fails

$|\beta^{(app)}| < \beta$

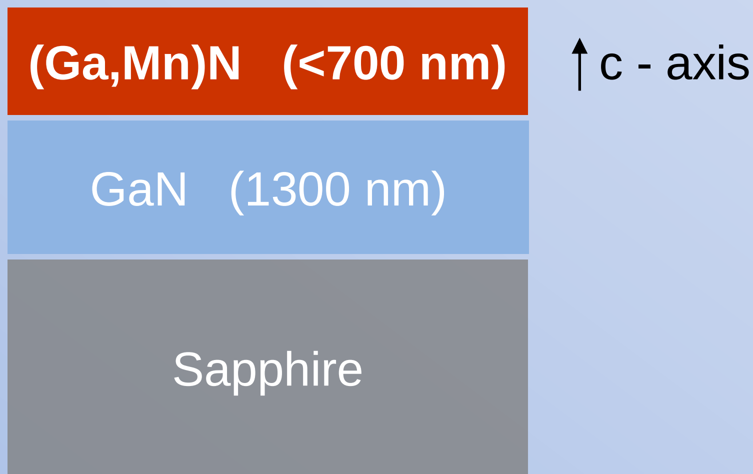
$\beta^{(app)} > 0$

$\alpha^{(app)}$ *reduced*

T. Dietl, PRB (2008).
C. Śliwa and T. Dietl, PRB (2008).

Samples

(Ga,Mn)N



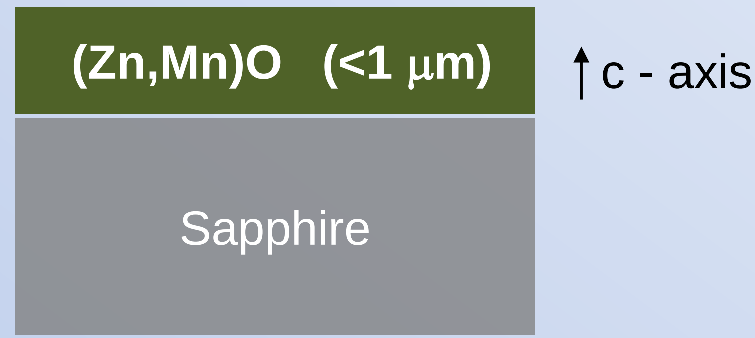
x_{Mn} < 0.9 % (SQUID and SIMS)

MOVPE grown (one series)

from:

J. Kepler University, Linz, Austria

(Zn,Mn)O



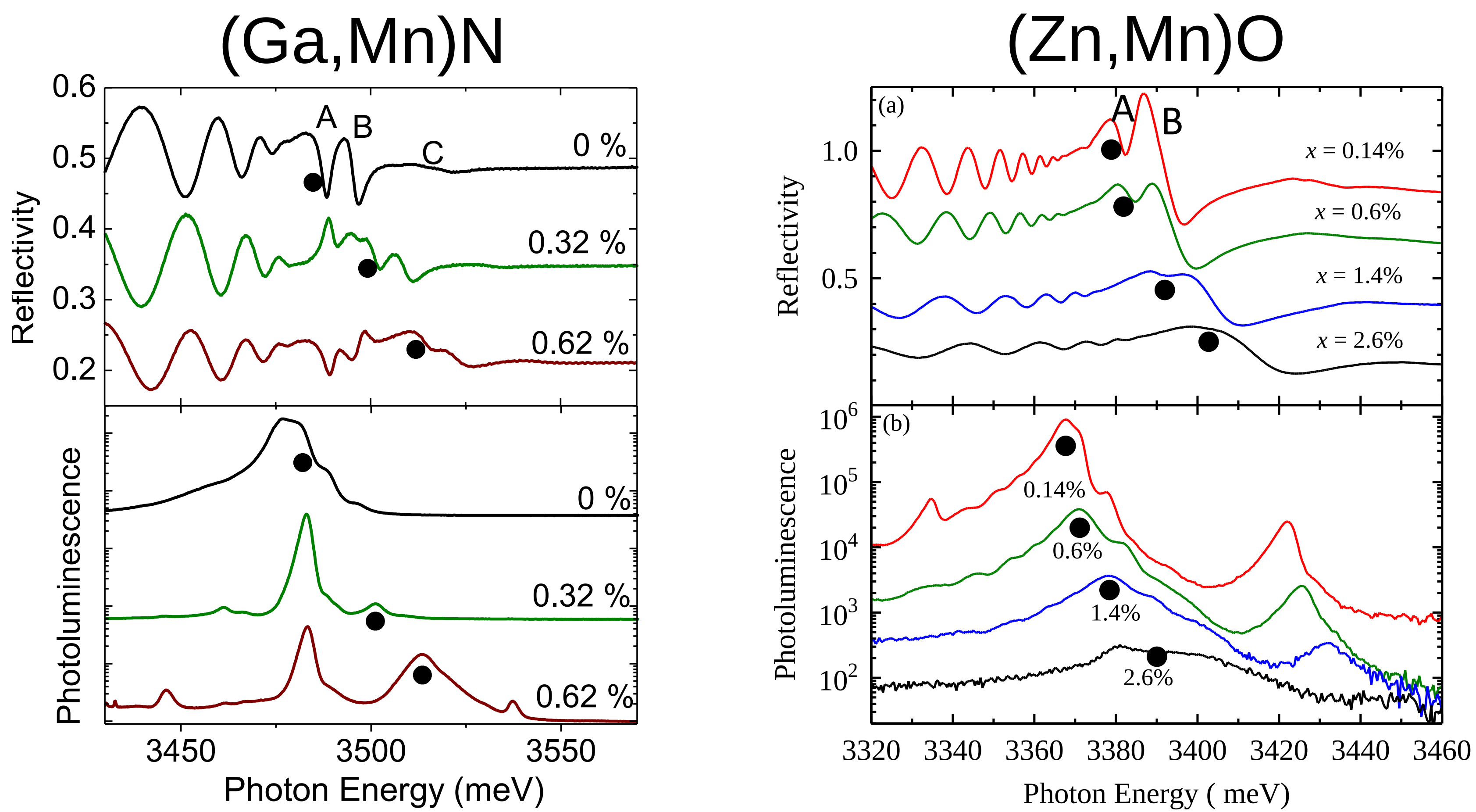
x_{Mn} < 3 % (SIMS)

MOCVD or MBE grown

from:

CNRS-Université de Versailles, Meudon, France
CNRS, Valbonne, France

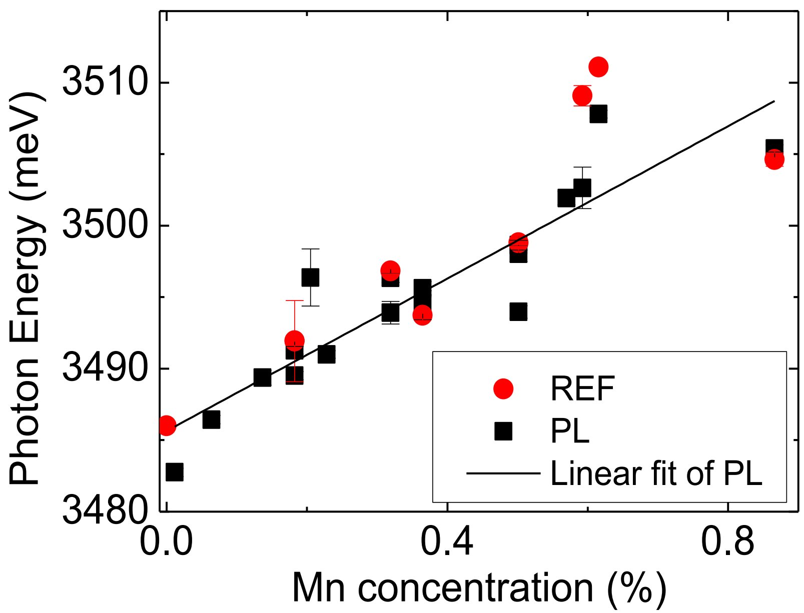
Zero field spectroscopy



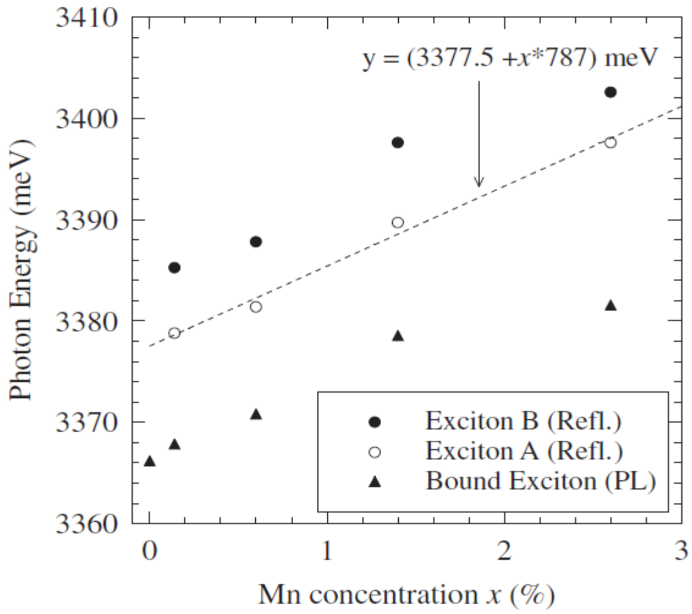
- Well resolved excitonic transitions in reflectivity
- Excitons shift towards higher energies with increasing Mn content

Band gap energy vs Mn concentration

(Ga,Mn)N



(Zn,Mn)O

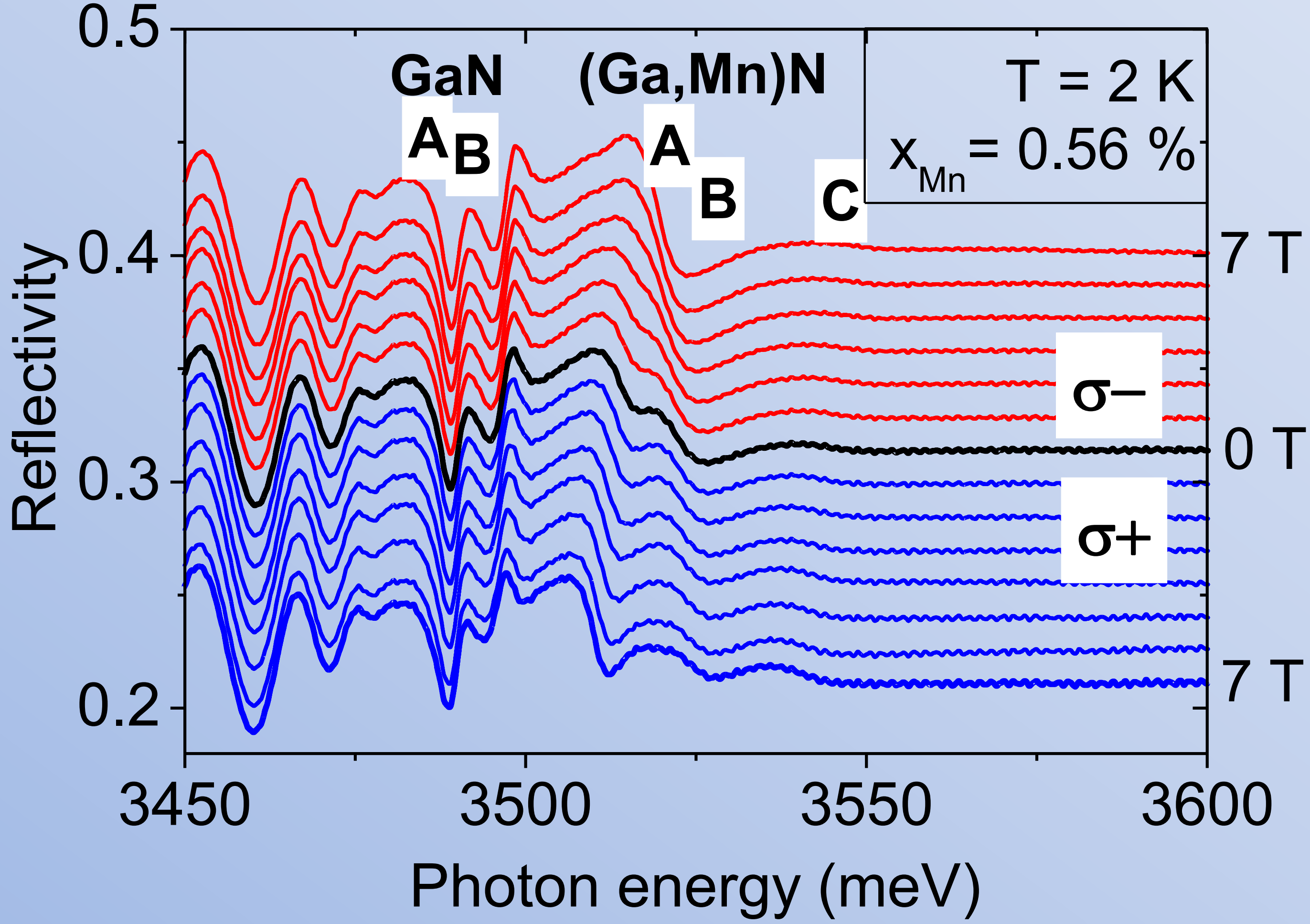


→ Increase of the band gap with increasing Mn concentration:

(contrary to e. g. ZnMnSe case)

in agreement with the recent theoretical predictions

Reflectivity in magnetic field – (Ga,Mn)N



- Reflectivity in magnetic field confirms identification of excitonic transitions
- Well resolved excitonic shifts

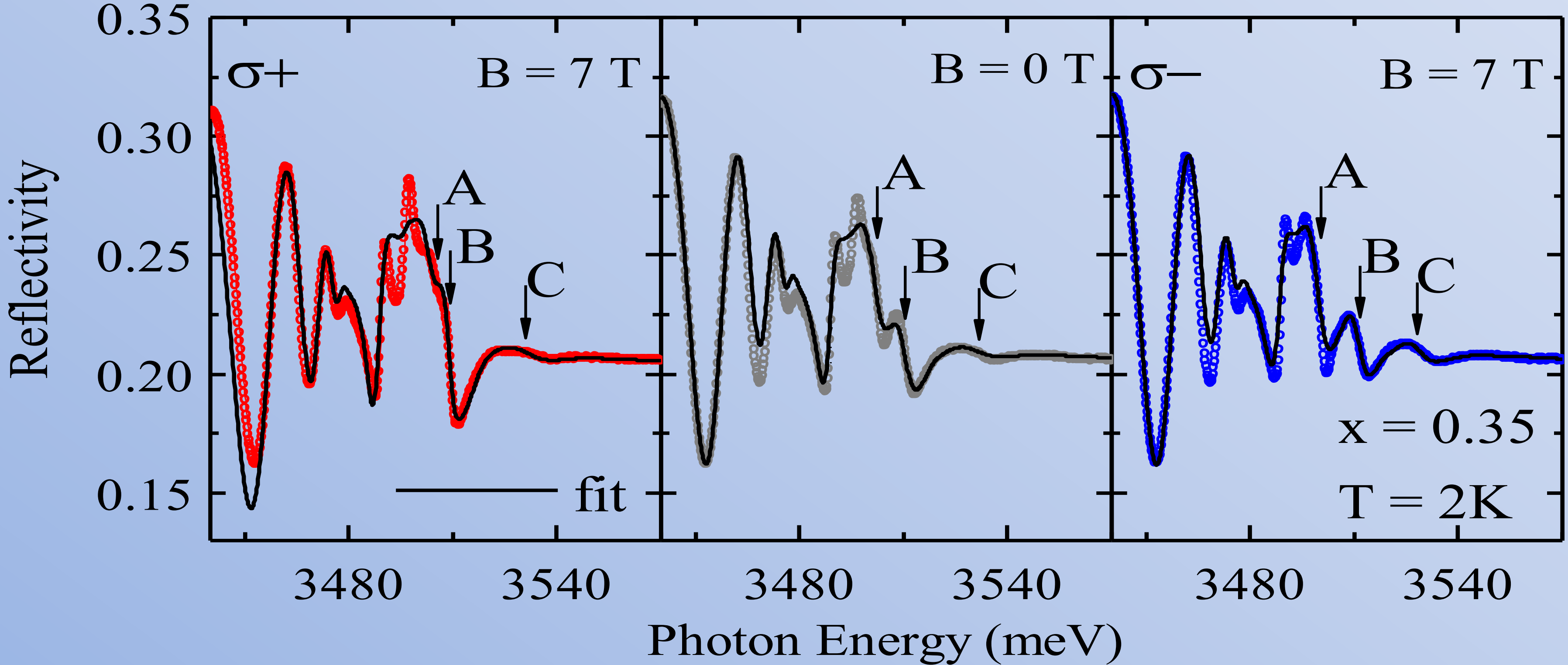
Model of the Reflectivity spectra

Dielectric function for GaN and (Ga,Mn)N layers:

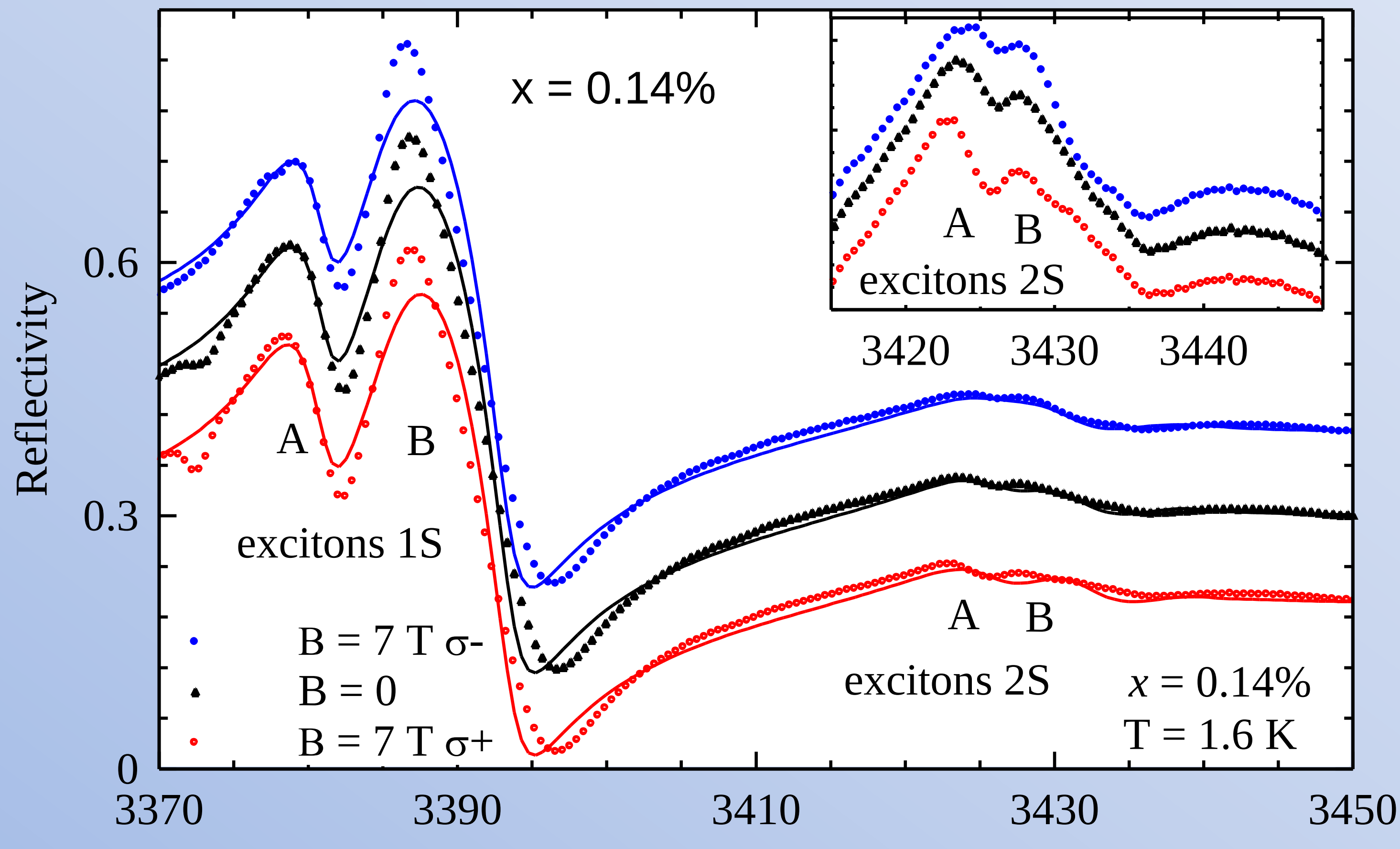
$$\varepsilon_j(E) = \varepsilon_0 + \frac{4\pi \cdot \alpha_{Aj} \cdot E_{Aj}^2}{(E_{Aj}-E)^2 - i \cdot E \cdot \Gamma_{Aj}} + \frac{4\pi \cdot \alpha_{Bj} \cdot E_{Bj}^2}{(E_{Bj}-E)^2 - i \cdot E \cdot \Gamma_{Bj}} + \frac{4\pi \cdot \alpha_{Cj} \cdot E_{Cj}^2}{(E_{Cj}-E)^2 - i \cdot E \cdot \Gamma_{Cj}} +$$

$$+ excitonic\ \ excited\ states + continuum\ \ of\ \ unbound\ states$$

Fitting parameters: energies, widths and polarizabilites of excitons A, B, C:



Reflectivity in magnetic field – (Zn,Mn)O



- Clear observation of the giant Zeeman splitting of 1S and 2S excitons
- Correct model description

Modelling of the of the excitonic shifts in magnetic field

Effective Hamiltonian:

$$H = E_0 + H_V + H_{e-h} + H_{s,p-d} + H_{Zeeman} + H_{dia}$$

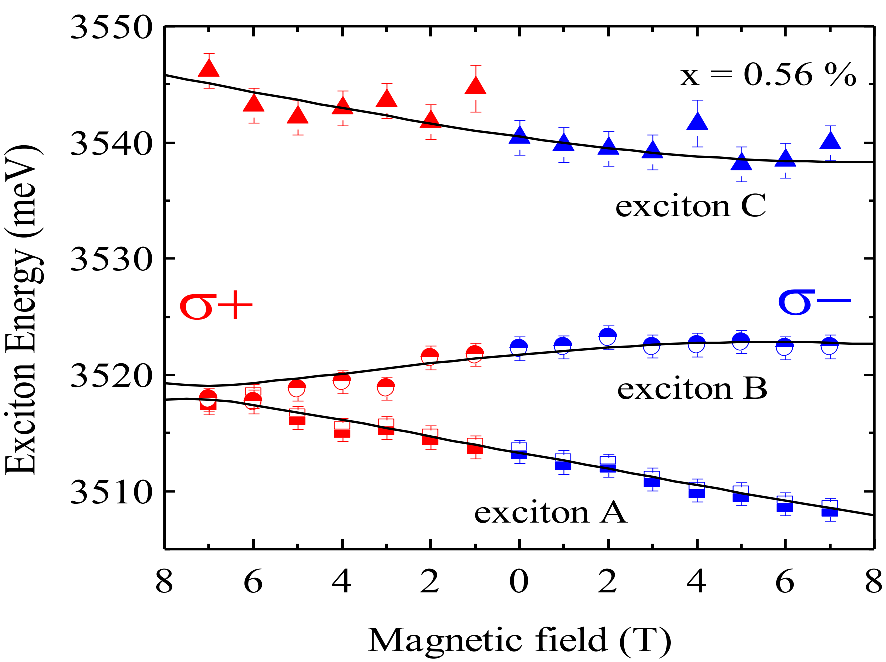
Hamiltonian of exchange interaction between Mn^{3+} ions and free carriers:

$$H_{s,p-d}^{\sigma\pm} = \pm\frac{1}{2} N_0 x_{Mn} \langle -S_Z \rangle \begin{pmatrix} \beta - \alpha & 0 & 0 \\ 0 & \alpha - \beta & 0 \\ 0 & 0 & \alpha + \beta \end{pmatrix}$$

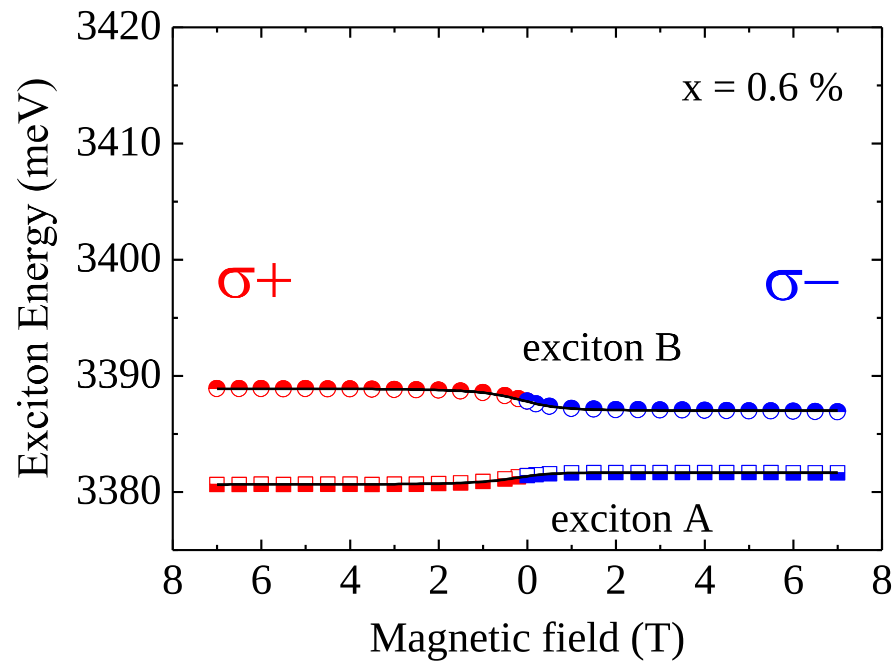
→Free parameters of the fit: $N_0\alpha$, $N_0\beta$, band gap energy, splittings Δ_1, Δ_2

Excitonic splitting in magnetic field

(Ga,Mn)N



(Zn,Mn)O

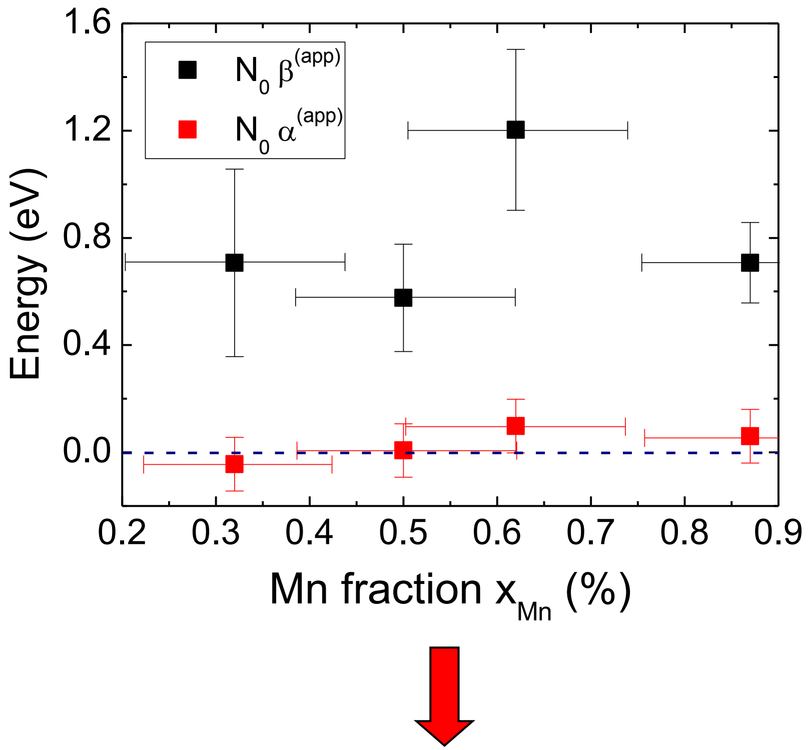


- Quantitative description of excitonic shifts in magnetic field
- Anticrossing of A and B excitons due to e-h exchange interaction
- Magnitude of A and B exciton splittings:

  → exciton A in (Zn,Mn)O has Γ_7 symmetry

Exchange constants

(Ga,Mn)N



$N_0\beta^{(app)}$ = + 0.8 ± 0.2 eV

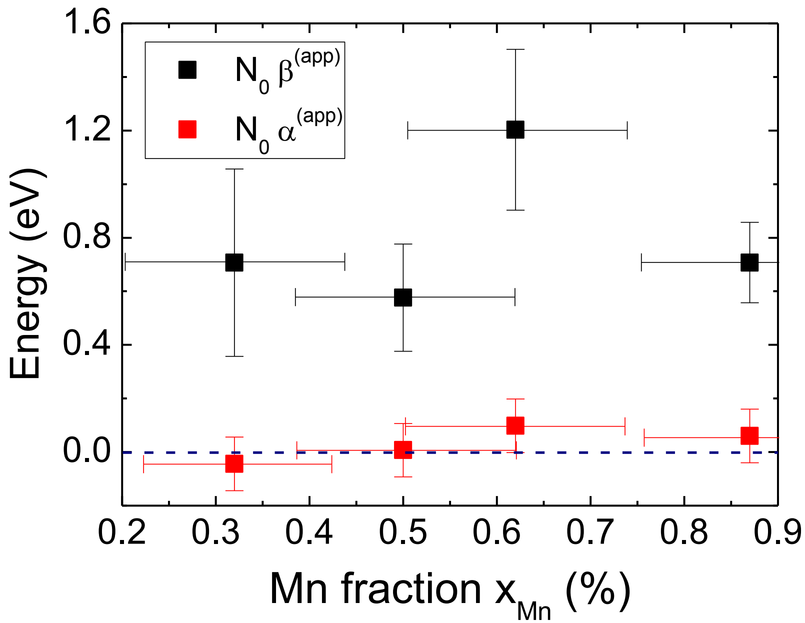
$N_0\alpha^{(app)}$ = 0.0 ± 0.1 eV

- *Apparent* $N_0\beta^{(app)}$ - reduced and ferromagnetic
- *Apparent* $N_0\alpha^{(app)}$ in (Ga,Mn)N - small

} as expected from the recent theories

Exchange constants

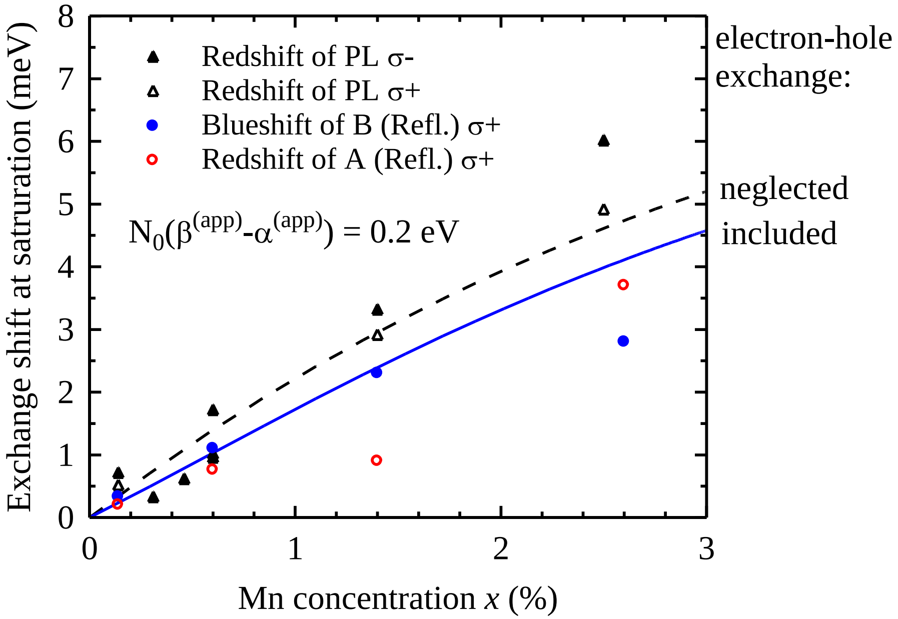
(Ga,Mn)N



$N_0\beta^{(app)} = +\,0.8 \pm 0.2$ eV

$N_0\alpha^{(app)} = \ \ 0.0 \pm 0.1$ eV

(Zn,Mn)O



$N_0(\beta^{(app)}-\alpha^{(app)}) = +\,0.2$ eV and $N_0\alpha^{(app)} = +\,0.3$ eV

$N_0\beta^{(app)} = +\,0.5$ eV

- *Apparent* $N_0\beta^{(app)}$ - reduced and ferromagnetic
- *Apparent* $N_0\alpha^{(app)}$ in (Ga,Mn)N - small

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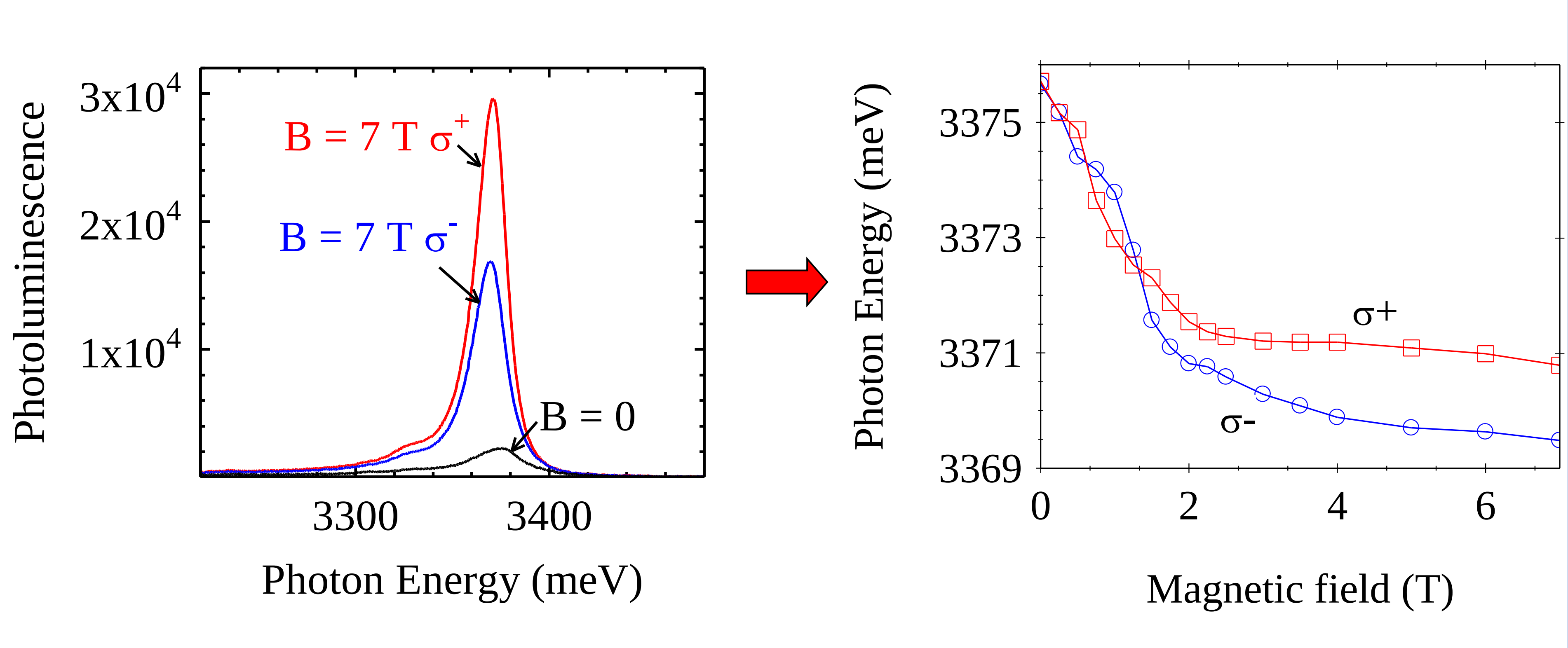
Photoluminescence in magnetic field – (Zn,Mn)O



- No e-h exchange → no exciton anticrossing
- Γ_9 shift larger than Γ_7 shift

Conclusions

- Band gap of (Ga,Mn)N and (Zn,Mn)O increases with Mn concentration
- *Apparent p-d* exchange energies $N_0\beta$ much reduced and ferromagnetic:

$N_0\beta^{(app)}$ = + 0.8 ± 0.2 for (Ga,Mn)N and + 0.5 ± 0.15 eV for (Zn,Mn)O

- *Apparent* s-d exchange energy in (Ga,Mn)N small: $N_0a^{(app)}$= + 0.0± 0.1 eV
- Opposite circular polarization of reflectivity in ZnO as compared to GaN

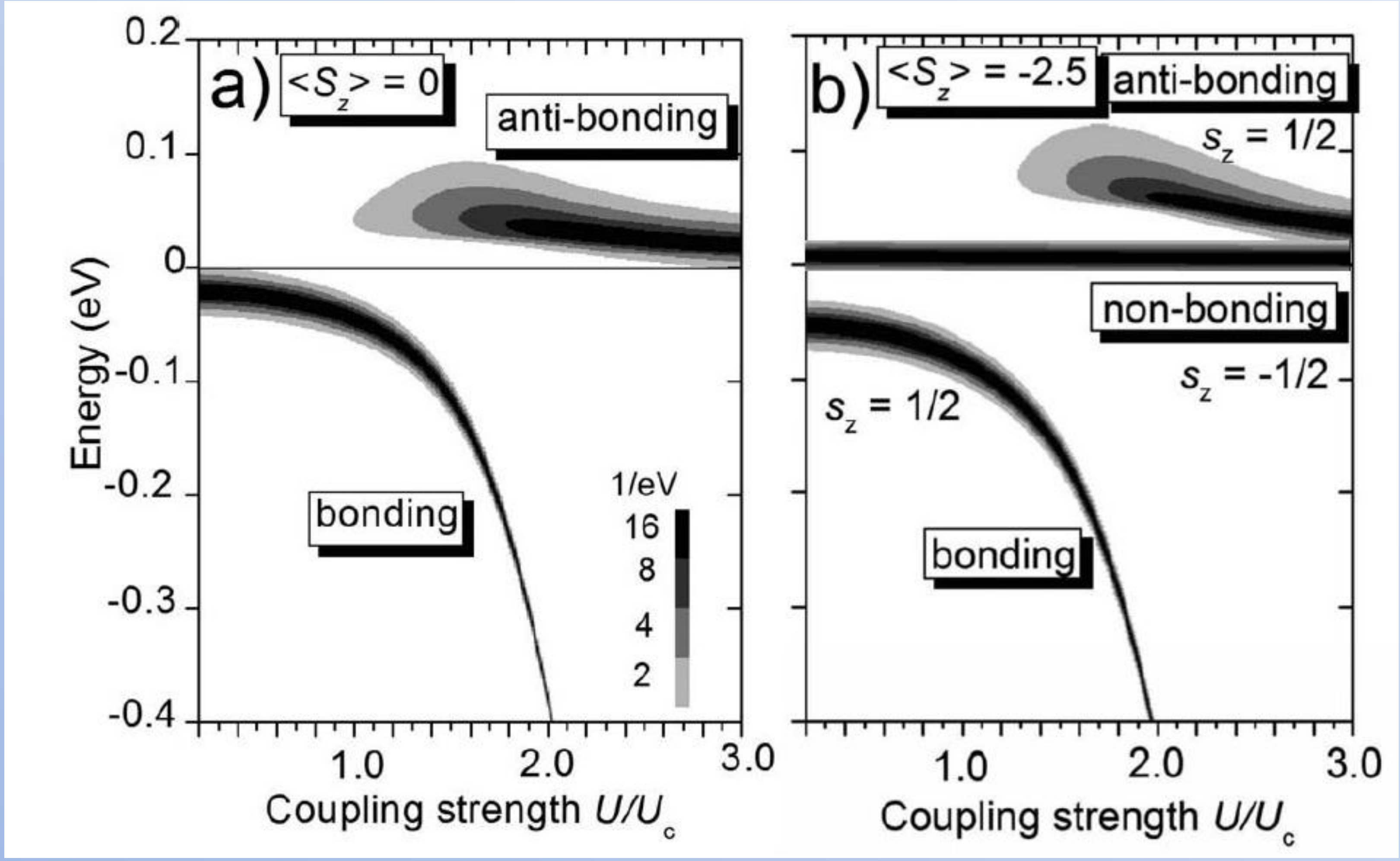
  due to reversed valence band ordering

→ Recent models /T. Dietl, PRB (2008).; C. Śliwa and T. Dietl, PRB (2008)./ of wide gap DMSs confirmed

- Mutually opposite polarization of excitonic photoluminescence and

reflectivity from (Zn,Mn)O explained

Strong coupling regime



Dietl, PRB'08